Selenium-Containing Heterocycles from Isoselenocyanates: Synthesis of 1,2,3-Selenadiazole Derivatives

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The reaction of aroyl chlorides **1** with KSeCN and ethyl diazoacetate (**6**) in acetone at room temperature yields ethyl 2-aroyl-5-(aroylimino)-2,5-dihydro-1,2,3-selenadiazole-4-carboxylates **7** (*Scheme 3*). A reaction mechanism *via* the initial formation of the corresponding aroyl isoselenocyanates **2** followed by a 1,3-dipolar cycloaddition of the diazo compound with the C=Se bond to give ethyl 5-(aroylimino)-4,5-dihydro-1,2,3-selenadiazole-4-carboxylates of type **D** is proposed. Acylation of the latter at N(2) leads to the final products **7**. Deacetylation of **7** to give ethyl 5-(aroylimino)-1,2,3-selenadiazole-4-carboxylates **10** is achieved by treatment of **7** with morpholine (*Scheme 5*). The intermediate isoselenocyanates **2** partially oligomerize to give two different oligomers. The symmetrical one reacts with morpholine to yield selenourea derivatives **12** (*Scheme 6*).

Introduction. – Selenium-containing heterocycles are of increasing interest because of their chemical properties [1] and biological activities [2]. Selenium compounds show broad similarities with the corresponding sulfur analogues, *e.g.*, they offer applications in the syntheses of dyes, pharmaceuticals, and fine chemicals. On the other hand, remarkable differences are known between Se- and S-compounds. Because of the larger size of the Se-atom, selenium compounds show an increased polarizability and, therefore, they are, in general, less stable than the S-analogues. Their physical properties make selena-heterocycles attractive materials in the development of organo-electric or organo-optic materials.

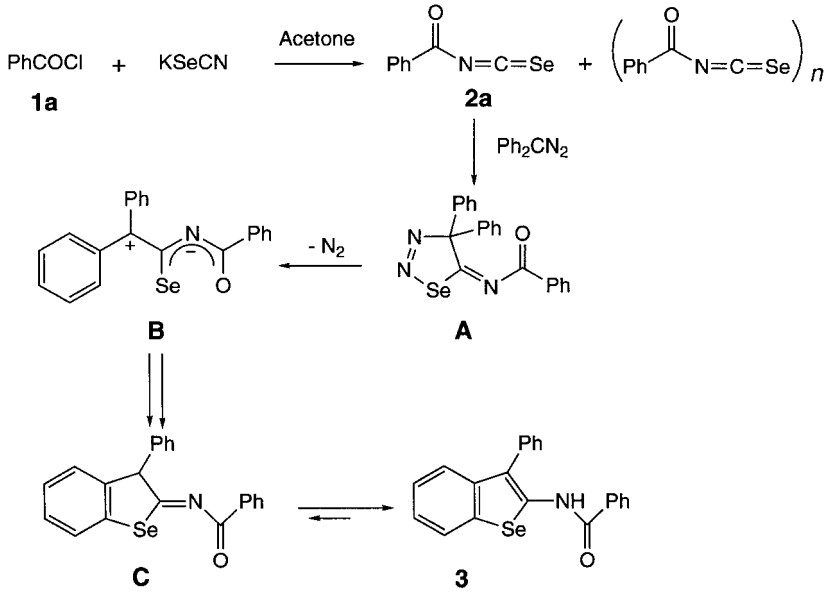
In spite of the obvious attractivity of Se-heterocycles, only a few preparative routes have been described [1][3] in comparison with sulfur heterocycles. In addition to the lower stability of the products, the high toxicity of the Se-containing starting materials seems to be the main drawback in the development of the chemistry of selena-heterocycles. Therefore, new approaches to organoselenium compounds from stable and less toxic Se-precursors are of current interest. Organic isoselenocyanates seem to meet these requirements as reagents for the preparation of Se-heterocycles [4] as well as of noncyclic Se-compounds, such as selenoureas, selenosemicarbazides, *etc.* [5], which again can be used in heterocyclic synthesis.

Aryl and alkyl isoselenocyanates are, in general, more difficult to prepare than aroyl isoselenocyanates. Whereas the synthesis of the former needs two or more reaction steps [6–8], the latter can easily be prepared by the reaction of aroyl chlorides **1** with potassium selenocyanide, a method first investigated by *Douglas* [9]. Although the aroyl isoselenocyanates of type **2** were never isolated or characterized, their reactions with amines to yield selenoureas [9] indicated the existence of these

[1]) Postdoctoral stay at the University of Zurich, 08.98–12.99.

intermediates. It was assumed that a polymeric form is present in equilibrium with the monomer that undergoes the observed reactions [10]. Although it is now well-accepted that benzoyl isoselenocyanate (**2a**) prepared by the method of *Douglas* [9] is a transient species, there is only one known example, so far, in which **2a** has been used as a dipolarophile for the synthesis of selenaheterocycles [4] (*Scheme 1*). On treatment of the crude **2a**, prepared *in situ* by the reaction of benzoyl chloride (**1a**) and KSeCN, with diphenyldiazomethane, *L'abbé et al.* obtained benzoselenophene **3** in 27% yield [4]. A conceivable mechanism for its formation *via* cycloadduct **A**[2]), elimination of N_2 to give zwitterion **B** (or the corresponding biradical), ring closure and aromatization to **C**, and tautomerization to yield **3** is shown in *Scheme 1*.

Scheme 1

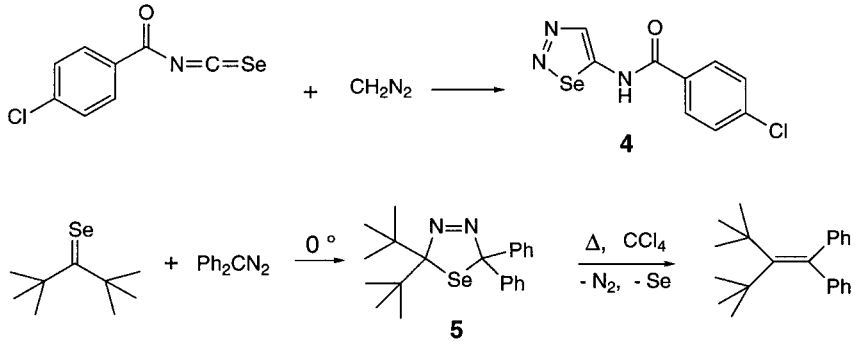


A second example of a reaction between an isoselenocyanate and a diazo compound is shown in *Scheme 2* [11]. In this case, the primarily formed cycloadduct **4** has been isolated. It should be noted that the 1,3-dipolar cycloaddition occurs regioselectively to give the 1,2,3-selenadiazole derivative. On the other hand, the reaction of di(*tert*-butyl) selenoketone with diphenyldiazomethane at 0° yields the 2,5-dihydro-1,3,4-selenadiazole **5** [13], which, on heating in CCl_4, undergoes a 'two-fold extrusion' (*cf.* [14]) to give 1,1-di(*tert*-butyl)-2,2-diphenylethene (*Scheme 2*).

In contrast to the few known examples of reactions of diazo compounds with isoselenocyanates and selenoketones, numerous examples of 1,3-dipolar cycloadditions with analogous C=S compounds have been reported [12][15]. For example, the well

[2]) The regioselectivity of the cycloaddition is formulated in analogy to the reaction of 4-chlorobenzoyl-isoselenocyanate with CH_2N_2 [11] (*Scheme 2*) and numerous cycloadditions of diazo compounds with isothiocyanates (*cf.* [12] and refs. cit. therein).

Scheme 2



known reaction of isothiocyanates with diazomethane, the so-called *Pechmann* reaction [16], leads to 1,2,3-thiadiazole derivatives (*cf.* [15])[3]). On the other hand, diazomethane and aliphatic thioketones in apolar solvents react to give preferentially or exclusively 1,3,4-thiadiazoles, but in polar solvents, the ratio of the isomers is shifted towards the 1,2,3-thiadiazoles [24][25][4]). All known reactions of ethyl diazoacetate (**6**) and 'non-cumulated' thiocarbonyl compounds proceeded *via* the formation of the corresponding 1,3,4-thiadiazoles (*cf.* [25][26] and refs. cit. therein).

As aroyl isoselenocyanates of type **2** are easily prepared, we intended to use them as dipolarophiles in 1,3-dipolar cycloadditions. In analogy with reactions of corresponding isothiocyanates (*cf.* [27]), we expected that the addition should occur exclusively and regioselectively at the C=Se bond. In the present paper, we report on the reactions with **6**.

Results. – The reaction of aroyl chlorides **1** with a mixture of KSeCN and ethyl diazoacetate (**6**) in dry acetone at room temperature led to 5-imino-1,2,3-selenadiazole-4-carboxylates of type **7** in moderate yields (*Scheme 3*). In all reactions, considerable amounts of structurally unknown oligomers of the intermediate isoselenocyanates were formed that did not react with **6** even after longer reaction times[5]). The structures of the products **7** were deduced from their analytical[6]) and spectral data, and, in the case of **7b**, the structure was confirmed by X-ray crystallography (*Figure*).

For instance, the CI-MS of **7b** shows a peak at m/z 458 ($[M+1]^+$), in accordance with the formula $C_{21}H_{19}N_3O_4Se$. The peak for the fragment ion m/z 340 with the characteristic Se isotope pattern, which results

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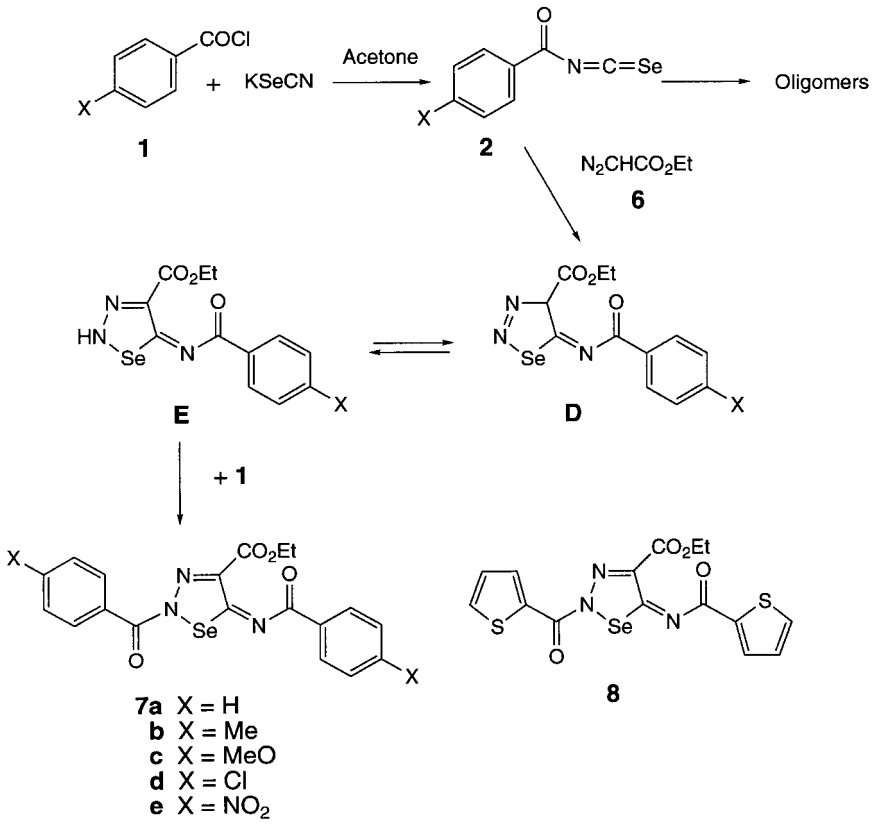
[3]) Recently, selenocarbonyl compounds have been used as dienophiles in hetero-*Diels-Alder* reactions [17–21]. It has been shown by *Sauer* and co-workers [18] that selenones react about 10 times faster with 1,3-dienes than the corresponding thioketones, which are called 'superdienophiles'. The reactions of 4,4′-dimethoxyselenobenzophenone with acetylenecarboxylates leading to 1*H*-benzo[*c*]selenopyranes were also interpreted as hetero-*Diels-Alder* reactions, with the selenocarbonyl compounds as the heterodiene [22] (*cf.* also [23]).

[4]) For example, the ratio of 1,3,4- and 1,2,3-thiadiazole derivatives formed from diazomethane and adamantanethione was 87:13 in petroleum ether, 58:42 in CH_2Cl_2, and 22:78 in MeOH [24a].

[5]) On the other hand, treatment of the oligomeric material with secondary amines yielded the corresponding selenourea derivatives (*vide infra*).

[6]) The compounds showed correct elemental analyses (±0.3%).

Scheme 3



from splitting off an aroyl moiety, is also observed. This is actually a common feature for all compounds of type **7**. Strong absorptions at 1720, 1702, 1682, and 1664 for C=O and C=N groups are present in the IR spectrum (KBr). In the ^{1}H-NMR spectrum ($CDCl_3$), the H_{ortho}-atoms of the 4-methylbenzoyl residues absorb as parts of two *AA′BB′* systems at 8.39 and 8.12 ppm, whereas the H_{meta}-atoms absorb as a *d*-like signal at 7.32 ppm. The signals of the ethoxy group appear at 4.57 (*q*) and 1.52 ppm (*t*), and the two Me signals are at 2.45 and 2.43 ppm; the corresponding signals in the ^{13}C-NMR spectrum appear at 62.1 (CH_2) and 21.9, 21.8, and 14.3 ppm (Me). At low field, five *s* between 178 and 144 ppm can be assigned to the sp^2-C-atoms bearing heteroatoms.

The crystal structure of **7b** shows a nearly planar molecule. The heterocyclic core and the (4-methylbenzoyl)imino group at C(5) form a planar system with the maximum deviation from the plane being 0.044(4) Å for C(14)[7]). The plane of the other 4-methylbenzoyl ring at N(2) makes an angle of 16.4° with this plane. The Se–O(19) distance is *ca.* 0.35 Å longer than the Se–C(5) and Se–N(2) bonds, but O(19) is still close enough to be considered to have a strong interaction with the Se-atom. The C(19)–O(19) carbonyl bond is correspondingly slightly longer than normal (*Table 1*). The O–Se interaction could be described as a dative bond. This arrangement could also favor a resonance structure **7B**

[7]) The arbitrary numbering of the atoms shown in the *Figure* is used.

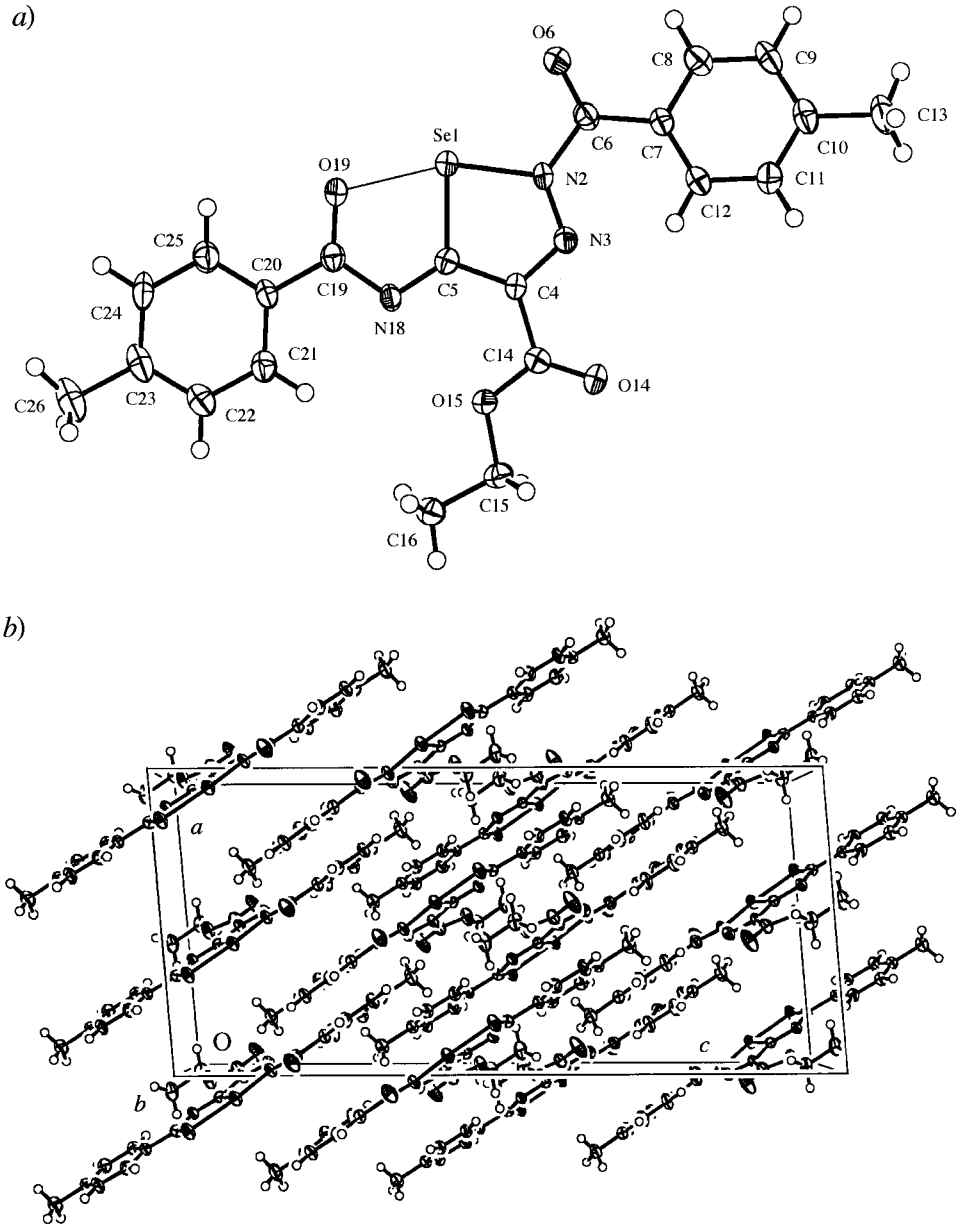
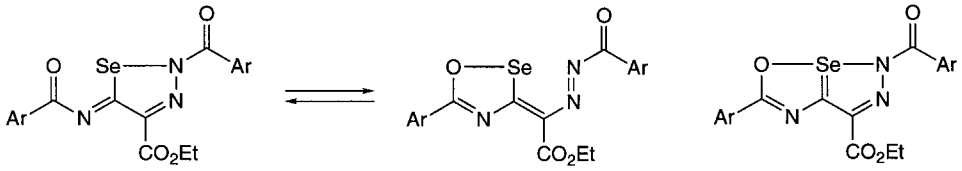


Figure. a) *ORTEP Plot* [28] *of the molecular structure of* **7b** (arbitrary numbering of the atoms; 50% probability ellipsoids) *and* b) *packing diagram*

or structure **7C** with a hypervalent Se-atom, although the N–C bond lengths give preference to a more localized depiction (**7A**)[8]).

Table 1. *Selected Bond Lengths* [Å] *of* **7b**

Se(1)–O(19)	2.242(2)	N(2)–C(6)	1.421(4)
Se(1)–N(2)	1.915(3)	N(3)–C(4)	1.324(4)
Se(1)–C(5)	1.878(3)	N(18)–C(5)	1.312(4)
O(6)–C(6)	1.211(4)	N(18)–C(19)	1.373(4)
O(14)–C(14)	1.200(4)	C(4)–C(5)	1.440(4)
O(19)–C(19)	1.259(4)	C(4)–C(14)	1.494(4)
N(2)–N(3)	1.313(3)		

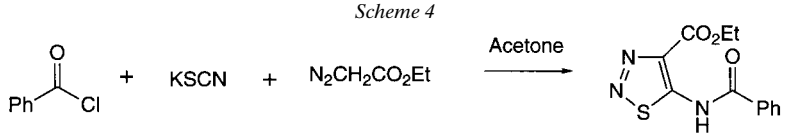


7A **7B** **7C**

The analogous reaction of thiophene-2-carbonyl chloride with KSeCN in the presence of **6** gave the corresponding thiophene derivative **8** in 25% yield (*Scheme 3*).

It was interesting that no 1:1 adduct of type **D** or **E** could be detected, even when the acid chloride and KSeCN were used in a 1:1 ratio. Therefore, the acylation of intermediate **E** must be a fast reaction. On the other hand, the analogous reaction of **1a** with KSCN yielded only the 1:1 adduct **9** (*cf.* [32])[9]) (*Scheme 4*), irrespective of whether 1 or 2 equiv. of **1a** were used. Obviously, selenadiazoles of type **E** are much more nucleophilic than their sulfur analogues.

Scheme 4



1a **6** **9**

Treatment of CH_2Cl_2 solutions of **7** and **8** with 1 equiv. of morpholine at room temperature led to ethyl 1,2,3-selenadiazole-4-carboxylates **10** and **11**, respectively, in 90–98% yield as crystalline products (*Scheme 5*). The structures were determined on the basis of the analytical[6]) and spectral data.

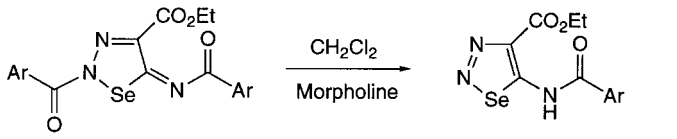
For example, the EI-MS of **10b** shows the peak for $M^{+\cdot}$ at *m/z* 339 and two main fragment ions at *m/z* 283 ($[M - C_2H_4 - N_2]^{+\cdot}$) and 267 ($[M - C_3H_4O_2]^{+}$). In the IR spectrum, there is an NH absorption at 3259 cm^{-1} and only one strong absorption in the C=O/C=N region (1670 cm^{-1}). The ^{1}H-NMR spectrum ($CDCl_3$) shows the

[8]) For the discussion of comparable structures, see [29]. Of special interest are the structures of some thia-, selena-, and tellurapentalenes that correspond to structure **7C** [30][31]. Non-bonded S,O and Se,O interactions of potential biological importance have been studied in thiazole and selenazole nucleosides [2d].

[9]) Previously, compound **9** has been prepared analogously to the *Pechmann* reaction (*cf.* [16]) with ethyl diazoacetate (**6**) and benzoyl isothiocyanate [32].

NH signal at 12.32 ppm, an *AA′BB′* system at 7.96 and 7.38 ppm, and a *s* at 2.47 ppm for the tolyl residue as well as a *q* (4.61 ppm) and a *t* (1.54 ppm) for the EtO group. The ^{13}C-NMR spectrum also shows undoubtedly that the molecule contains only one tolyl group.

Scheme 5

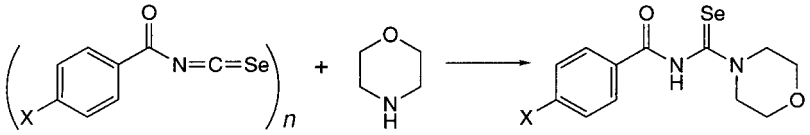


7a–e, 8

10a Ar = Ph
b Ar = 4-MeC_6H_4
c Ar = 4-$MeOC_6H_4$
d Ar = 4-ClC_6H_4
e Ar = 4-$NO_2C_6H_4$
11 Ar = 2-thienyl

To get more information about the oligomers of the isoselenocyanates, we treated the crude mixtures of the oligomers[10]) in CH_2Cl_2 with morpholine. The only products that could be isolated and characterized were the corresponding yellowish and crystalline *N*-aroylselenoureas **12** (*Scheme 6*)[11]). Surprisingly, the yields of **12** varied strongly with the substituent X and also between different experiments (95% to $<20\%$). We concluded that only one of the oligomers in the mixture underwent the reaction with morpholine, whereas the other did not.

Scheme 6



12a X = H
b X = Me
c X = MeO
d X = Cl
e X = NO_2

Therefore, the mixture of oligomers was separated by fractional crystallization from CH_2Cl_2, and one component was obtained in pure form[12]). The reaction of this

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[10]) The ^{1}H-NMR spectra of these mixtures showed, in general, three kinds of aroyl moieties, *e.g.*, in the case of the oligomer of **2b**, three *s* for aromatic Me groups are present (2.47, 2.46, and 2.43 ppm). The intensities of the signals at 2.47 and 2.43 ppm were always equal, whereas the ratio with the *s* at 2.46 ppm varied considerably. Correspondingly, the signals of the H-atoms of the 4-methylphenyl substituents also showed that there are three kinds of tolyl residues present, two of them always showing the same intensities, whereas the ratio to the third moiety varied between different batches. This observation could be rationalized by assuming the presence of two oligomers of the isoselenocyanates, one of them containing two nonequivalent aroyl moieties and the second one with a symmetric structure ('symmetric' oligomer: 8.26 (*AA′BB′*, $J=8.2$, arom. H); 7.33 (*AA′BB′*, $J=8.0$, arom. H); 2.46 (*s*, Me); 'asymmetric' oligomer: 8.38, 7.87 (2*AA′BB′*, $J=8.2$, 8.3, arom. H); 7.37, 7.31 (2*AA′BB′*, $J=8.0$, 7.9, arom. H); 2.47, 2.43 (2*s*, Me)).

[11]) In addition, in all cases a red-orange compound of unknown structure was detected by TLC.

[12]) This oligomer, the 'symmetric' one, showed only one type of aroyl group; *e.g.*, in the case of the oligomer of **2b**, a single *s* for an aromatic Me group was detected at 2.46 ppm.

oligomer with morpholine led in all cases to the corresponding selenourea **12** in high and reproducible yields of 82–98%. In contrast to the reaction with the crude oligomer, there was no red-orange compound formed[13])[14]).

Discussion. – The described reaction of aroyl chlorides **1** with KSeCN in the presence of excess ethyl diazoacetate (**6**) yields ethyl 2-aroyl-5-(aroylimino)-1,2,3-selenadiazole-4-carboxylates **7** (*Scheme 3*). The formation of the product can be rationalized by a 1,3-dipolar cycloaddition of the diazo compound with the *in situ* generated isoselenocyanide of type **2**. In addition, part of the latter reacts to give a mixture of oligomers. The speed with which the aroyl chloride is added dropwise to the solution of KSeCN and **6** in acetone seems to be important with respect to the yield of product **7**, as quick addition leads to bigger amounts of oligomers and lower yields of **7**. This observation can be interpreted by considering that during the slow addition of **1**, only low concentrations of the transient **2** were produced and, therefore, the oligomerization is disfavored.

The highest yields of **7** were obtained when 1.2–1.4 equiv. of **1** and 1.3–3 equiv. of **6**, with respect to KSeCN, were used. A larger excess of **6** did not increase the yield of **7**. More surprising was the result that an increase of the ratio **1**/KSeCN to 2:1, *i.e.*, the stoichiometric ratio, lowered the yield of **7**. We propose that several side reactions, of which the oligomerization of the transient **2** is one, are responsible for the disappearance of the material. Furthermore, using the aroyl chloride in a larger excess made the workup of the mixture more difficult and, therefore, led to lower yields of isolated products.

In contrast to the analogous reaction with diphenyldiazomethane [4] (*cf. Scheme 1*), no N_2 elimination from the primarily formed cycloadduct was observed. A conceivable explanation could be a different regioselectivity of the cycloaddition[15]). As established by X-ray crystallography, in our case the final products **7** and, therefore, the primarily formed intermediates **D**, are 1,2,3-selenadiazole derivatives. This regioselectivity is in accordance with that observed in 1,3-dipolar cycloadditions of diazo compounds with isothiocyanates [16] and other compounds with cumulated C=S bonds [12] and with the reaction of **1a**, KSCN, and **6** (*cf. Scheme 4*). It can be assumed that 4,5-dihydro-1,2,3-selenadiazoles are thermally more stable than the isomeric 2,5-dihydro-1,3,4-selenadiazoles, in analogy to the well-documented thermal stabilities of the corresponding thiadiazoles[15]). With this trend in mind, the formation of **3** (*Scheme 1*) *via* an intermediate 2,5-dihydro-1,3,4-selenadiazole **F** should also be taken into consideration (*Scheme 7*). The elimination of N_2 would lead to a selenocarbonyl ylide, which undergoes a ring closure to give selenirane **G**. A ring enlargement of the latter *via* the zwitterion **B** (or the corresponding biradical) leads to **3**. Another – and more likely –

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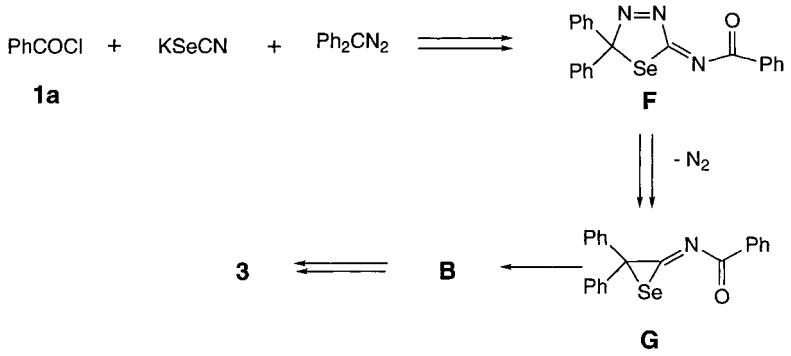
[13]) A red crystalline compound, identified as 2-(benzoylamino)-5-(diethylamino)-1,6,6aλ^4-triselena-3,4-diazapentalene, was also isolated by *Köhler et al.* from the reaction of KSeCN with benzoyl chloride and Et_2NH [31].

[14]) In the case of the reaction of KSeCN with thiophene-2-carbonyl chloride, a pure oligomer containing two nonequivalent thiophenecarbonyl moieties (^{1}H-NMR) was isolated. Its reaction with morpholine yielded no selenourea but only a red-yellow compound. The details of this reaction will be reported later.

[15]) In the case of 1,3-dipolar cycloadducts of diazo compounds with thioketones, a smooth elimination of N_2 to give thiocarbonyl ylides as reactive intermediates is observed only with the 2,5-dihydro-1,3,4-thiadiazoles, whereas the isomeric 4,5-dihydro-1,2,3-thiadiazoles proved to be more stable [24a][33].

explanation for the higher stability of the 1,2,3-selenadiazole derivatives **D** (*Scheme 3*) compared with **A** (*Scheme 1*) is the effect of the substituents. In the case of 2,5-dihydro-1,3,4-thiadiazoles it has been shown that phenyl substituents reduce the thermal stability, whereas electron-withdrawing substituents increase it [24a]. Therefore, it can be expected that **D** is more stable than **A**. Furthermore, in contrast to **A**, the primarily formed cycloadduct **D** can tautomerize to **E**, which can be trapped by acylation with **1**.

Scheme 7



The oligomeric isoselenocyanates can easily be isolated by treating the reaction mixture with CH_2Cl_2 or $CHCl_3$; the insoluble solid was a mixture of two oligomers which could be separated chromatographically. The presence of different oligomers, a 'symmetric' and an 'unsymmetric' one, was clearly indicated by the NMR spectra[10]). Although the structures of these compounds are not known, it was shown that in each case, the 'symmetric' oligomer reacted with morpholine to give the corresponding selenourea derivative of type **12** in high yield, whereas the 'unsymmetric' oligomers failed to undergo this reaction but led to yellow-red compounds of unknown structures. Based on this observation, the moderate yields of aroylselenoureas achieved in previous works, in which the crude mixture of oligomers of the corresponding isoselenocyanates have been used for the reaction with amines [10][31], are understandable.

In conclusion, we have shown that 1,2,3-selenadiazole-4-carboxylates **7** and **8**, as well as **10** and **11**, are easily accessible by the reaction of ethyl diazoacetate (**6**) with *in situ* generated aroyl isoselenocyanates of type **2**. In this protocol, the Se-atom is introduced by using KSeCN as a cheap and safe Se-source[16]). All other 1,2,3-selenadiazoles described up to date have been prepared by the method of *Lalezari et al.* by the oxidation of aryl benzyl ketone semicarbazones with SeO_2 [35] (*cf.* [36]).

We thank the analytical units of our institute for spectra and analyses, and Dr. *A. Linden* for performing the X-ray crystal-structure determination. Financial support of this work by the *Dr. Helmut Legerlotz Stiftung* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

[16]) For the use of KSeCN for the synthesis of arenecarboselenoamides, see [34].

Experimental Part

1. *General*. TLC: silica gel *60* F_{254} plates (0.25 mm; *Merck*); hexane/AcOEt 1:1 or 2:1 as eluents. Column chromatography (CC): silica gel *60* (0.040–0.063 mesh; *Merck*). M.p.: *Büchi B-540* apparatus; in capillary; uncorrected. IR Spectra: *Perkin-Elmer 1600-FT-IR* spectrophotometer; in KBr, absorption bands in cm^{-1}. ^{1}H-NMR (300 or 600 MHz) and ^{13}C-NMR (75.5 or 150.9 MHz) spectra: *Bruker ARX-300* and *Bruker AMX-600* instrument; in $CDCl_3$, unless otherwise stated; chemical shifts in ppm, coupling constants J in Hz; ^{13}C-signal multiplicities from DEPT spectra. EI- and CI-MS: *Finnigan SSQ-700* or *MAT-90* instrument; EI mode, 70 eV; CI mode, NH_3 as carrier gas.

2. *Ethyl 2-Aroyl-5-(aroylimino)-2,5-dihydro-1,2,3-selenadiazole-4-carboxylates* **7** *and* **8**: *General Procedure*. To a stirred soln. of KSeCN (0.02 mol) and ethyl diazoacetate (**6**; 0.03–0.04 mol) in dry acetone (30–40 ml), a soln. of the corresponding aroyl chloride (0.024–0.028 mmol) in acetone (25–30 ml) was slowly added at r.t. (0.05–0.1 ml/min). After further stirring for 1–2 h, the mixture was poured into H_2O (400 ml) and stirred for an additional hour. The precipitate was filtered by suction, air-dried, and dissolved with CH_2Cl_2 or $CHCl_3$. The soln. was treated with charcoal and then concentrated. The products **5** and **6** precipitated as yellowish fibrous crystals. The yields are calculated with respect to the half molar amount of aroyl chloride.

Ethyl 2-Benzoyl-5-(benzoylimino)-2,5-dihydro-1,2,3-selenadiazole-4-carboxylate (**7a**): 1.62 g (32%). Yellowish crystals. M.p. 123.0–123.5° (Et_2O). IR: 2973*w*, 1728*s*, 1680*s*, 1598*w*, 1587*m*, 1542*s*, 1496*w*, 1466*m*, 1447*m*, 1370*m*, 1345*m*, 1314*m*, 1252*s*, 1179*s*, 1168*s*, 1115*m*, 1069*w*, 1027*m*, 1000*w*. ^{1}H-NMR: 8.52 (*d*, J = 7.1, 2 arom. H); 8.19 (*d*, J = 7.1, 2 arom. H); 7.67–7.60 (*m*, 3 arom. H); 7.56–7.51 (*m*, 3 arom. H); 4.57 (*q*, J = 7.1, CH_2); 1.51 (*t*, J = 7.1, *Me*CH_2). ^{13}C-NMR: 178.8, 174.2, 169.1, 160.4, 143.0 (5*s*, 3 C=O, 2 C=N); 133.8, 133.4, 131.6, 130.5, 128.7, 128.3 (6*d*, 10 arom. CH); 132.9, 130.2 (2*s*, 2 arom. C); 62.1 (*t*, CH_2); 14.2 (*q*, *Me*CH_2). CI-MS: 430 (100, $[M+1]^+$), 326 (48). Anal. calc. for $C_{19}H_{15}N_3O_4Se$ (428.31): C 53.27, H 3.50, N 9.81; found: C 53.22, H 3.64, N 9.79.

Ethyl 2-(4-Methylbenzoyl)-5-[(4-methylbenzoyl)imino]-2,5-dihydro-1,2,3-selenadiazole-4-carboxylate (**7b**): 2.00 g (35%). Yellowish crystals. M.p. 153.5–154.0° (CH_2Cl_2/Et_2O). IR: 2982*w*, 1720*s*, 1702*m*, 1682*m*, 1664*w*, 1605*m*, 1582*w*, 1535*s*, 1490*m*, 1460*m*, 1410*w*, 1371*m*, 1343*m*, 1312*m*, 1256*s*, 1173*s*, 1110*m*, 1043*w*, 1020*m*. ^{1}H-NMR: 8.39 (*AA*′BB′, J = 8.2, 2 arom. H); 8.12 (*AA*′BB′, J = 8.3, 2 arom. H); 7.32 (2 AA′*BB*′, J = 8.4, 4 arom. H); 4.57 (*q*, J = 7.1, CH_2); 2.45, 2.43 (2*s*, 2 Me); 1.52 (*t*, J = 7.1, *Me*CH_2). ^{13}C-NMR: 178.7, 173.8, 168.9, 160.6, 144.9, 144.5, 142.7 (7*s*, 3 C=O, 2 C=N, 2 arom. C); 131.8, 130.6, 129.6, 129.2 (4*d*, 8 arom. CH); 130.5, 127.4 (2*s*, 2 arom. C); 62.1 (*t*, CH_2); 21.9, 21.8 (2*q*, 2 Me); 14.3 (*q*, *Me*CH_2). CI-MS: 458 (100, $[M+1]^+$), 340 (19). Anal. calc. for $C_{21}H_{19}N_3O_4Se$ (456.36): C 55.27, H 4.20, N 9.21; found: C 55.16, H 4.27, N 9.20.

Crystals suitable for the X-ray crystal-structure determination were grown from CH_2Cl_2/$CHCl_3$/acetone.

Ethyl 2-(4-Methoxybenzoyl)-5-[(4-methoxybenzoyl)imino]-2,5-dihydro-1,2,3-selenadiazole-4-carboxylate (**7c**): 2.25 g (38%). Yellowish crystals. M.p. 190.5–191.3° (CH_2Cl_2). IR: 2972*w*, 2937*w*, 2837*w*, 1720*s*, 1661*m*, 1604*s*, 1584*s*, 1556*s*, 1515*s*, 1478*m*, 1459*m*, 1420*w*, 1370*m*, 1348*m*, 1320*m*, 1244*s*, 1194*s*, 1159*s*, 1115*s*, 1021*s*. ^{1}H-NMR: 8.47 (*AA*′BB′, J = 9.0, 2 arom. H); 8.28 (*AA*′BB′, J = 9.1, 2 arom. H); 7.01 (2 AA′*BB*′, J = 8.8, 4 arom. H); 4.58 (*q*, J = 7.1, CH_2); 3.904, 3.898 (2*s*, 2 MeO); 1.52 (*t*, J = 7.1, *Me*CH_2). ^{13}C-NMR: 177.9, 173.2, 167.9, 164.2, 163.9, 142.3 (6*s*, 3 C=O, 2 C=N, 2 arom. C); 134.1, 132.7, 114.0, 113.8 (4*d*, 8 arom. CH); 125.8, 122.3 (2*s*, 2 arom. C); 62.0 (*t*, CH_2); 55.5 (*q*, 2 MeO); 14.3 (*q*, *Me*CH_2). CI-MS: 490 (100, $[M+1]^+$), 356 (37). Anal. calc. for $C_{21}H_{19}N_3O_6Se$ (488.36): C 51.64, H 3.89, N 8.61; found: C 51.25, H 3.92, N 8.57.

Ethyl 2-(4-Chlorobenzoyl)-5-[(4-chlorobenzoyl)imino]-2,5-dihydro-1,2,3-selenadiazole-4-carboxylate (**7d**): 2.36 g (42%). Yellowish crystals. M.p. 226.5–227.5° (CH_2Cl_2). IR: 1737*s*, 1670*s*, 1582*s*, 1539*s*, 1493*m*, 1468*m*, 1400*m*, 1376*m*, 1315*s*, 1262*s*, 1190*s*, 1172*s*, 1117*m*, 1094*s*, 1014*s*. ^{1}H-NMR: 8.45 (*AA*′BB′, J = 8.6, 2 arom. H); 8.17 (*AA*′BB′, J = 8.8, 2 arom. H); 7.521, 7.517 (2 AA′*BB*′, J = 8.7, 8.6, 4 arom. H); 4.57 (*q*, J = 7.1, CH_2); 1.51 (*t*, J = 7.1, *Me*CH_2). ^{13}C-NMR: 177.9, 174.4, 168.0, 160.2, 143.1, 140.4, 140.2 (7*s*, 3 C=O, 2 C=N, 2 arom. C); 133.0, 131.8, 129.1, 128.7 (4*d*, 8 arom. CH); 131.3, 128.4 (2*s*, 2 arom. C); 62.3 (*t*, CH_2); 14.2 (*q*, *Me*CH_2). CI-MS: 498 (100, $[M+1]^+$), 360 (83). Anal. calc. for $C_{19}H_{13}Cl_2N_3O_4Se$ (497.20): C 45.88, H 2.62, Cl 14.09, N 8.45; found: C 45.77, H 2.64, Cl 14.49, N 8.49.

Ethyl 2,5-Dihydro-2-(4-nitrobenzoyl)-5-[(4-nitrobenzoyl)imino]-1,2,3-selenadiazole-4-carboxylate (**7e**): 2.10 g (41%). Yellowish crystals. M.p. 248.0–249.0° (CH_2Cl_2). IR: 3116*w*, 1732*s*, 1698*m*, 1602*w*, 1535*s*, 1458*m*, 1409*m*, 1345*s*, 1322*m*, 1265*s*, 1203*s*, 1169*m*, 1108*m*, 1013*m*. ^{1}H-NMR: 8.72 (*AA*′BB′, J = 8.9, 2 arom. H); 8.42 (*AA*′BB′, J = 8.9, 2 arom. H); 8.36 (2 AA′*BB*′, J = 8.9, 4 arom. H); 4.61 (*q*, J = 7.1, CH_2); 1.53 (*t*, J = 7.1, *Me*CH_2). ^{13}C-NMR: 177.6, 175.8, 168.0, 160.1, 151.2, 150.7, 144.3, 138.0, 135.8 (9*s*, 3 C=O, 2 C=N, 4 arom. C); 132.8, 131.8, 124.3, 123.7 (4*d*, 8 arom. CH); 62.9 (*t*, CH_2); 14.5 (*q*, *Me*CH_2). CI-MS: 520 (100 $[M+1]^+$), 371 (32). Anal. calc. for $C_{19}H_{13}N_5O_8Se$ (518.31): C 44.02, H 2.51, N 13.51; found: C 43.79, H 2.61, N 13.54.

Ethyl 2,5-Dihydro-2-(2-thienylcarbonyl)-5-[(2-thienylcarbonyl)imino]-1,2,3-selenadiazole-4-carboxylate (**8**): 1.32 g (25%). Yellowish crystals. M.p. 182.7–183.3° (acetone). IR: 3106*w*, 1728*s*, 1656*m*, 1551*s*, 1505*m*, 1469*m*, 1404*m*,

1348*s*, 1256*s*, 1223*m*, 1193*s*, 1099*m*, 1038*m*, 1018*m*. ^{1}H-NMR: 8.44 (*dd*, *J* = 3.9, 1.3, 1 arom. H); 8.21 (*dd*, *J* = 3.8, 1.3, 1 arom. H); 7.83 (*dd*, *J* = 5.0, 1.3, 1 arom. H); 7.75 (*dd*, *J* = 4.9, 1.3, 1 arom. H); 7.24 (*dd*, *J* = 4.0, 3.9, 1 arom. H); 7.22 (*dd*, *J* = 4.0, 3.9, 1 arom. H); 4.61 (*q*, *J* = 7.1, CH_2); 1.57 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 173.59, 173.56, 162.1, 160.2, 142.2, 138.5, 131.2 (7*s*, 3 C=O, 2 C=N, 2 C(thiophene)); 138.3, 137.5, 135.0, 134.8, 128.8, 127.8 (6*d*, 6 CH(thiophene)); 62.3 (*t*, CH_2); 14.4 (*q*, *Me*CH_2). EI-MS: 441 (0.7, $M^{+\cdot}$), 385 (0.6), 330 (0.4), 265 (0.8), 111 (100). Anal. calc. for $C_{15}H_{11}N_3O_4S_2Se$ (440.36): C 40.91, H 2.52, N 9.54, S 14.56; found: C 40.88, H 2.47, N 9.54, S 14.21.

3. *Ethyl 5-Benzamido-1,2,3-thiadiazole-4-carboxylate* (**9**). According to the *General Procedure* of *Sect. 2*, 1.61 g (25%) of **9** were obtained. Yellowish crystals. M.p. 183.5–184.0° (CH_2Cl_2). IR: 3289*m*, 3062*w*, 2990*w*, 1670*s*, 1599*m*, 1581*w*, 1518*s*, 1465*m*, 1407*m*, 1380*m*, 1356*w*, 1300*s*, 1259*s*, 1214*s*, 1104*w*, 1068*w*, 1028*s*. ^{1}H-NMR: 11.73 (*s*, NH); 8.05 (*d*-like, *J* = 7.0, 2 arom. H); 7.70 (*t*-like, *J* = 7.4, 1 arom. H); 7.59 (*t*-like, *J* = 7.4, 2 arom. H); 4.62 (*q*, *J* = 7.1, CH_2); 1.54 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 164.1, 163.9, 156.4, 138.0, 129.9 (5*s*, 2 C=O, 1 arom. C, C(4), C(5)); 134.0, 129.3, 127.8 (3*d*, 5 arom. CH); 62.4 (*t*, CH_2); 14.2 (*q*, *Me*CH_2). CI-MS: 278 ($[M+1]^+$). Anal. calc. for $C_{12}H_{11}N_3O_3S$ (277.31): C 51.98, H 4.00, N 15.15, S 11.56; found: C 52.12, H 4.11, N 15.01, S 11.76.

4. *Ethyl 5-(Aroylamino)-1,2,3-selenadiazole-4-carboxylates* **10** *and* **11**: *General Procedure.* To a stirred soln. of **7** or **8** (5 mmol) in CH_2Cl_2 (60 ml) at r.t., an equimolar amount of morpholine was added dropwise. The product precipitated partially. The mixture was concentrated and filtered by suction, and the colorless solid washed with Et_2O.

Ethyl 5-(Benzoylamino)-1,2,3-selenadiazole-4-carboxylate (**10a**): 1.56 g (96%). Colorless crystals. M.p. 215.0–216.0° (CH_2Cl_2). IR: 3259*m*, 3060*m*, 2990*m*, 1662*s*, 1598*m*, 1579*w*, 1508*s*, 1464*m*, 1453*m*, 1432*m*, 1400*m*, 1374*m*, 1337*s*, 1254*s*, 1212*s*, 1189*m*, 1108*w*, 1062*w*, 1026*m*. ^{1}H-NMR: 12.40 (*s*, NH); 8.07 (*d*, *J* = 7.5, 2 arom. H); 7.70 (*t*, *J* = 7.4, 1 arom. H); 7.60 (*t*, *J* = 7.4, 2 arom. H); 4.62 (*q*, *J* = 7.1, CH_2); 1.54 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 164.7, 163.9, 161.4, 139.5, 129.9 (5*s*, 2 C=O, 1 arom. C, C(4), C(5)); 134.0, 129.3, 127.9 (3*d*, 5 arom. CH); 62.3 (*t*, CH_2); 14.3 (*q*, *Me*CH_2). EI-MS: 325 (1.0, $M^{+\cdot}$), 269 (7.5), 267 (3.2), 253 (2.1), 105 (100), 77 (45.6). Anal. calc. for $C_{12}H_{11}N_3O_3Se$ (324.20): C 44.46, H 3.42, N 12.96; found: C 44.36, H 3.47, N 12.97.

Ethyl 5-[(4-Methylbenzoyl)amino]-1,2,3-selenadiazole-4-carboxylate (**10b**): 1.55 g (92%). Colorless crystals. M.p. 182.7–183.3° (CH_2Cl_2/Et_2O). IR: 3220*m*, 2986*w*, 2938*w*, 1671*s*, 1607*m*, 1571*w*, 1523*s*, 1505*s*, 1467*m*, 1440*m*, 1412*m*, 1370*s*, 1261*s*, 1222*s*, 1188*m*, 1122*m*, 1073*w*, 1029*s*. ^{1}H-NMR: 12.32 (*s*, NH); 7.96 (*AA′*BB′, *J* = 8.3, 2 arom. H); 7.38 (AA′*BB′*, *J* = 8.3, 2 arom. H); 4.61 (*q*, *J* = 7.1, CH_2); 2.47 (*s*, Me); 1.54 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 164.7, 163.7, 161.4, 145.2, 139.4, 127.0 (6*s*, 2 C=O, 2 arom. C, C(4), C(5)); 130.0, 127.9 (2*d*, 4 arom. CH); 62.2 (*t*, CH_2); 21.7 (*q*, Me); 14.3 (*q*, *Me*CH_2). EI-MS: 339 (0.6, $M^{+\cdot}$), 283 (8.7), 281 (3.9), 267 (2.4), 119 (100), 91 (52.3). Anal. calc. for $C_{13}H_{13}N_3O_3Se$ (338.23): C 46.16, H 3.87, N 12.42; found: C 45.98, H 3.95, N 12.38.

Ethyl 5-[(4-Methoxybenzoyl)amino]-1,2,3-selenadiazole-4-carboxylate (**10c**): 1.68 g (95%). Colorless crystals. M.p. 194.0–194.5° (CH_2Cl_2). IR: 3243*w*, 2990*w*, 2967*w*, 2937*w*, 2904*w*, 1667*s*, 1604*s*, 1574*s*, 1527*s*, 1510*s*, 1474*m*, 1446*s*, 1416*m*, 1399*m*, 1372*s*, 1349*s*, 1252*s*, 1221*s*, 1181*s*, 1117*m*, 1069*w*, 1026*s*. ^{1}H-NMR: 12.28 (*s*, NH); 8.02 (*AA′*BB′, *J* = 8.9, 2 arom. H); 7.05 (AA′*BB′*, *J* = 8.9, 2 arom. H); 4.61 (*q*, *J* = 7.1, CH_2); 3.91 (*s*, MeO); 1.54 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 164.7, 164.2, 163.2, 161.6, 139.2, 122.0 (6*s*, 2 C=O, 2 arom. C, C(4), C(5)); 130.0, 114.6 (2*d*, 4 arom. CH); 62.2 (*t*, CH_2); 55.6 (*q*, MeO); 14.3 (*q*, *Me*CH_2). EI-MS: 355 (0.5, $M^{+\cdot}$), 299 (5.7), 297 (2.5), 283 (1.4), 135 (100). Anal. calc. for $C_{13}H_{13}N_3O_4Se$ (354.23): C 44.08, H 3.70, N 11.86; found: C 43.82, H 3.80, N 11.79.

Ethyl 5-[(4-Chlorobenzoyl)amino]-1,2,3-selenadiazole-4-carboxylate (**10d**): 1.67 g (93%). Colorless crystals. M.p. 217.0–217.5° (CH_2Cl_2). IR: 3280*m*, 2978*m*, 1663*s*, 1595*s*, 1572*m*, 1522*s*, 1493*m*, 1472*m*, 1448*s*, 1405*m*, 1377*m*, 1345*s*, 1306*m*, 1261*s*, 1215*s*, 1184*m*, 1116*m*, 1093*s*, 1028*m*, 1010*m*. ^{1}H-NMR: 12.39 (*s*, NH); 8.00 (*AA′*BB′, *J* = 8.7, 2 arom. H); 7.57 (AA′*BB′*, *J* = 8.7, 2 arom. H); 4.62 (*q*, *J* = 7.1, CH_2); 1.54 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 164.7, 162.9, 161.3, 140.7, 139.6, 128.3 (6*s*, 2 C=O, 2 arom. C, C(4), C(5)); 129.7, 129.2 (2*d*, 4 arom. CH); 62.4 (*t*, CH_2); 14.3 (*q*, *Me*CH_2). EI-MS: 359 (0.8, $M^{+\cdot}$), 303 (8.8), 301 (3.9), 287 (2.4), 141 (31.6), 139 (100), 111 (37.2). Anal. calc. for $C_{12}H_{10}ClN_3O_3Se$ (358.65): C 40.19, H 2.81, Cl 9.90, N 11.72; found: C 40.03, H 2.85, Cl 9.88, N 11.71.

Ethyl 5-[(4-Nitrobenzoyl)amino]-1,2,3-selenadiazole-4-carboxylate (**10e**): 1.75 g (95%). Colorless crystals. M.p. 276° (dec., CH_2Cl_2). IR: 3272*m*, 3110*w*, 2985*w*, 1669*s*, 1603*m*, 1523*s*, 1473*m*, 1449*m*, 1408*m*, 1380*m*, 1343*s*, 1323*s*, 1301*m*, 1259*s*, 1218*s*, 1160*w*, 1116*w*, 1080*w*, 1024*m*, 1011*m*. ^{1}H-NMR: 12.59 (*s*, NH); 8.45 (*AA′*BB′, *J* = 8.7, 2 arom. H); 8.25 (AA′*BB′*, *J* = 8.7, 2 arom. H); 4.63 (*q*, *J* = 7.1, CH_2); 1.55 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 164.8, 162.2, 161.0, 150.9, 139.9, 135.3 (6*s*, 2 C=O, 2 arom. C, C(4), C(5)); 129.1, 124.4 (2*d*, 4 arom. CH); 62.6 (*t*, CH_2); 14.3 (*q*, *Me*CH_2). EI-MS: 370 (1.6, $M^{+\cdot}$), 316 (2.2), 314 (12.0), 312 (5.6), 298 (3.1), 150 (100), 120 (14.3), 104 (44.4), 92 (19.7), 76 (27.5). Anal. calc. for $C_{12}H_{10}N_4O_5Se$ (369.22): C 39.04, H 2.73, N 15.17; found: C 39.00, H 2.75, N 15.26.

Ethyl 5-[(2-Thienylcarbonyl)amino]-1,2,3-selenadiazole-4-carboxylate (**11**): 1.48 g (90%). Yellowish crystals. M.p. 194° (dec., EtOH). IR: 3257*w*, 3063*m*, 2987*w*, 1661*s*, 1505*s*, 1441*s*, 1414*s*, 1345*s*, 1297*m*, 1259*s*, 1234*s*,

1204*s*, 1092*m*, 1072*m*, 1031*m*. ^{1}H-NMR: 12.23 (*s*, NH); 7.92 (*dd*, *J* = 3.9, 1.1, 1 arom. H); 7.77 (*dd*, *J* = 5.0, 1.1, 1 arom. H); 7.26 (*dd*, *J* = 5.0, 3.9, 1 arom. H); 4.61 (*q*, *J* = 7.1, CH_2); 1.54 (*t*, *J* = 7.1, *Me*CH_2). ^{13}C-NMR: 164.6, 161.1, 158.6, 134.6 (4*s*, 2 C=O, 1 C(thiophene), C(4), C(5)); 134.3, 131.3, 128.6 (3*d*, 3 CH(thiophene)); 62.3 (*t*, CH_2); 14.3 (*q*, *Me*CH_2). EI-MS: 331 (0.5, $M^{+\bullet}$), 275 (3.7), 273 (1.8), 259 (0.9), 257 (0.5), 111 (100). Anal. calc. for $C_{10}H_9N_3O_3SSe$ (330.23): C 36.37, H 2.75, N 12.72, S 9.71; found: C 36.44, H 2.81, N 12.64, S 9.82.

5. *Selenourea Derivatives* **12**: *General Procedure*. The mixture of oligomers of **2**, obtained as a by-product of the reaction described in *Sect. 2*, was triturated and recrystallized in $CHCl_3$ until the substance showed only one type of aroyl moiety in the ^{1}H-NMR spectrum ('symmetric oligomer'). Then, the oligomer (an amount which corresponded to 5 mmol of the monomer **2**) was suspended in CH_2Cl_2 (20 ml), and morpholine (5 mmol) was added dropwise to the stirred suspension at r.t. The precipitated **10** was filtered and washed with Et_2O.

N-*[(Morpholin-4-yl)selenocarbonyl]benzamide* (**12a**): 1.45 g (98%). Yellow-greenish crystals. M.p. 160° (dec., EtOH). IR: 3282*m*, 3031*m*, 2986*m*, 2940*m*, 2917*m*, 2881*m*, 1695*s*, 1600*m*, 1582*w*, 1523*s*, 1452*s*, 1422*s*, 1352*m*, 1313*m*, 1246*s*, 1224*s*, 1193*s*, 1176*s*, 1146*s*, 1110*s*, 1098*s*, 1078*m*, 1060*s*, 1020*s*. ^{1}H-NMR: 8.79 (br. *s*, NH); 7.85 (*d*, *J* = 7.2, 2 arom. H); 7.61 (*t*, *J* = 7.4, 1 arom. H); 7.50 (*t*, *J* = 7.5, 2 arom. H); 4.34, 3.90, 3.81, 3.80 (4 br. *s*, 4 CH_2). ^{13}C-NMR: 180.7, 161.7, 132.9 (3*s*, 1 C=O, 1 arom. C, 1 C=Se); 133.2, 128.9, 127.8 (3*d*, 5 arom. CH); 66.1, 65.9 (2*t*, 2 CH_2O); 55.2, 53.6 (2*t*, 2 CH_2N). EI-MS: 298 (16, $M^{+\bullet}$), 218 (5), 105 (100). Anal. calc. for $C_{12}H_{14}N_2O_2Se$ (297.22): C 48.49, H 4.75, N 9.43; found: C 48.17, H 4.74, N 9.38.

4-Methyl-N-*[(morpholin-4-yl)selenocarbonyl]benzamide* (**12b**): 1.45 g (93%). Yellowish crystals. M.p. 164° (dec., EtOH). IR: 3322*m*, 3030*w*, 2988*w*, 2961*w*, 2921*m*, 2866*m*, 1660*s*, 1610*m*, 1520*s*, 1455*s*, 1434*s*, 1386*m*, 1347*w*, 1320*w*, 1302*m*, 1262*s*, 1240*s*, 1224*m*, 1185*s*, 1143*s*, 1112*s*, 1062*m*, 1026*s*. ^{1}H-NMR: 8.73 (br. *s*, NH); 7.74 (*AA′*BB′, *J* = 8.3, 2 arom. H); 7.29 (AA′*BB′*, *J* = 8.5, 2 arom. H); 4.34, 3.90 (2 br. *s*, 2 CH_2O); 3.81, 3.64 (2 br. *s*, 2 CH_2N); 2.43 (*s*, Me). ^{13}C-NMR: 180.8, 161.7, 144.1, 129.2 (4*s*, 1 C=O, 2 arom. C, 1 C=Se); 129.6, 127.8 (2*d*, 4 arom. CH); 66.2, 65.9 (2*t*, 2 CH_2O); 55.2, 53.6 (2*t*, 2 CH_2N); 21.5 (*s*, Me). CI-MS: 313 (81, $[M+1]^+$), 233 (40). Anal. calc. for $C_{13}H_{16}N_2O_2Se$ (311.25): C 50.17, H 5.18, N 9.00; found: C 49.86, H 5.08, N 8.89.

4-Methoxy-N-*[(morpholin-4-yl)selenocarbonyl]benzamide* (**12c**): 1.40 g (91%). Yellowish crystals. M.p. 143.0–144.0° (acetone). IR: 3317*m*, 3023*w*, 2949*w*, 2923*m*, 2867*w*, 2833*w*, 1660*s*, 1610*m*, 1526*s*, 1512*s*, 1455*s*, 1434*s*, 1388*m*, 1348*w*, 1320*m*, 1303*m*, 1283*m*, 1260*s*, 1242*s*, 1225*m*, 1186*s*, 1176*s*, 1145*s*, 1112*s*, 1076*m*, 1062*m*, 1025*s*. ^{1}H-NMR: 8.71 (br. *s*, NH); 7.81 (*AA′*BB′, *J* = 8.9, 2 arom. H); 6.97 (AA′*BB′*, *J* = 9.0, 2 arom. H); 4.34, 3.90 (2 br. *s*, 2 CH_2O); 3.88 (*s*, MeO); 3.80, 3.62 (2 br. *s*, 2 CH_2N). ^{13}C-NMR: 180.9, 163.6, 161.3, 124.1 (4*s*, 1 C=O, 2 arom. C, 1 C=Se); 129.9, 114.2 (2*d*, 4 arom. CH); 66.2, 65.9 (2*t*, 2 CH_2O); 55.5 (*q*, MeO); 55.2, 53.6 (2*t*, 2 CH_2N). EI-MS: 328 (15, $M^{+\bullet}$), 135 (100). Anal. calc. for $C_{13}H_{16}N_2O_3Se$ (327.25): C 47.71, H 4.93, N 8.56; found: C 47.52, H 4.88, N 8.49.

4-Chloro-N-*[(morpholin-4-yl)selenocarbonyl]benzamide* (**12d**): 1.40 g (85%). Colorless crystals. M.p. 161° (dec., CH_2Cl_2). IR: 3442*w*, 3157*m*, 2977*m*, 2900*m*, 2873*m*, 1693*s*, 1588*s*, 1537*s*, 1460*s*, 1442*s*, 1398*m*, 1351*m*, 1301*m*, 1252*s*, 1212*s*, 1201*s*, 1175*s*, 1150*s*, 1114*s*, 1089*s*, 1062*m*, 1025*s*, 1010*s*. ^{1}H-NMR: 8.78 (br. *s*, NH); 7.79 (*AA′*BB′, *J* = 8.7, 2 arom. H); 7.47 (AA′*BB′*, *J* = 8.7, 2 arom. H); 4.33, 3.90 (2 br. *s*, 2 CH_2O); 3.80, 3.62 (2 br. *s*, 2 CH_2N). ^{13}C-NMR: 180.5, 160.8, 139.8, 130.3 (4*s*, 1 C=O, 2 arom. C, 1 C=Se); 129.3, 129.2 (2*d*, 4 arom. CH); 66.1, 65.9 (2*t*, 2 CH_2O); 55.2, 53.6 (2*t*, 2 CH_2N). EI-MS: 332 (13, $M^{+\bullet}$), 139 (100). Anal. calc. for $C_{12}H_{13}ClN_2O_2Se$ (331.66): C 43.46, H 3.95, Cl 10.69, N 8.45; found: C 43.21, H 3.97, Cl 10.70, N 8.42.

4-Nitro-N-*[(morpholin-4-yl)selenocarbonyl]benzamide* (**12e**): 1.40 mg (82%). Yellow crystals. M.p. 200° (dec., EtOH/acetone). IR: 3448*w*, 3118*m*, 2845*m*, 1694*s*, 1606*m*, 1537*s*, 1524*s*, 1460*s*, 1444*s*, 1349*s*, 1318*m*, 1253*s*, 1220*m*, 1192*s*, 1148*s*, 1115*s*, 1066*m*, 1027*m*, 1010*m*. ^{1}H-NMR: 8.75 (br. *s*, NH); 8.35 (*AA′*BB′, *J* = 8.9, 2 arom. H); 8.08 (AA′*BB′*, *J* = 8.9, 2 arom. H); 4.35, 3.92 (2 br. *s*, 2 CH_2O); 3.83, 3.64 (2 br. *s*, 2 CH_2N). ^{13}C-NMR: 180.0, 159.8, 150.5, 137.5 (4*s*, 1 C=O, 2 arom. C, 1 C=Se); 129.0, 124.2 (2*d*, 4 arom. CH); 66.2, 65.9 (2*t*, 2 CH_2O); 55.4, 53.8 (2*t*, 2 CH_2N). CI-MS: 344 (41, $[M+1]^+$), 264 (63). Anal. calc. for $C_{12}H_{13}N_3O_4Se$ (342.22): C 42.12, H 3.83, N 12.28; found: C 41.88, H 3.88, N 12.15.

6. *Crystal-Structure Determination of* **7b**[17]). All measurements were made on a *Rigaku AFC5R* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating anode generator. The ω scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction was applied [37]. Data collection and refinement

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[17]) Crystallographic data (excluding structure factors) for structure **7b** reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-137242. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

parameters are given in *Table 2*, a view of the molecule is shown in the *Figure*. The structure was solved by heavy-atom *Patterson* methods [38], which revealed the position of the Se-atom. All remaining non-H-atoms were located in a *Fourier* expansion of the *Patterson* solution with DIRDIF 94 [38]. The non-H-atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of the parent C-atom. Refinement of the structures was carried out on F with full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o|-|F_c|)^2$. A correction for secondary extinction was not applied. Neutral atom scattering factors for non-H-atoms were taken from [39a] and the scattering factors for H-atoms from [40]. Anomalous dispersion effects were included in F_c [41]; the values for f' and f'' were those of [39b], and the values of the mass attenuation coefficients were those of [39c]. All calculations were performed using the 'teXsan' crystallographic software package [42].

Table 2. *Crystallographic Data of Compound* **7b**

Crystallized from	CH_2Cl_2/$CHCl_3$/acetone
Empirical formula	$C_{21}H_{19}N_3O_4Se$
Formula weight [g mol^{-1}]	456.30
Crystal color, habit	yellow, prism
Crystal dimensions [mm]	0.35 × 0.30 × 0.28
Temp. [K]	173(1)
Crystal system	monoclinic
Space group	*C*2/*c*
Z	8
Reflections for cell determination	23
2θ Range for cell determination [°]	37 – 40
Unit-cell parameters *a* [Å]	12.018 (3)
b [Å]	12.447 (3)
c [Å]	27.010 (2)
β [°]	94.91 (1)
V [Å^3]	4025 (1)
D_x [g cm^{-3}]	1.506
μ(MoK_α) [mm^{-1}]	1.898
$2\theta_{(max)}$ [°]	55
Transmission factors (min; max)	0.889; 1.000
Total reflections measured	5063
Symmetry-independent reflections	4623
Reflections used [$I > 2\sigma(I)$]	3146
Parameters refined	262
Final *R*	0.0402
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0316
Goodness of fit	1.354
Final Δ_{max}/σ	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.38; – 0.44

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