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The Reactions of 2-(Bromoseleno)benzenesulfonyl Chloride with Primary Amines toward 2,2′-Diselenobis(benzenesulfonamides) and 1,3,2-Benzothiaselenazole 1,1-Dioxides: New Oxygen-Transfer Agents, Antimicrobials and Virucides

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The reaction of title compound **6** with primary aliphatic or aromatic amines was investigated. The products were 2,2′-diselenobis(benzenesulfonamides) (**4**) accompanied in some cases by 1,3,2-benzothiaselenazole 1,1-dioxides (**3**). Exceptionally, when aniline was a reagent, 2-(sulfamoylphenyl)phenylselenenylanilide was produced. These results are interpreted in the light of the proposed mechanisms. The compounds **3** and **4** exhibited catalytic activity in hydroperoxide oxidation of cyclohexanone (**12**) and 1-naphthaldehyde N,N-dimethylhydrazone (**17**). Although they were inactive against patogenic bacteria and fungi an appreciable antiviral activity against HSV-1 and EMCV of the compounds **3b**, **3c** and **4b** was observed.

Key words: amines, antimicrobials, oxidation, selenium compounds, virucides

Organoselenium compounds have been extensively applied in organic and material synthesis, ligand chemistry and biologically relevant processes [1–6]. Among them particular attention has been focused on benzisoselenazol-3(2H)ones (**1**) and their open-chain analogues 2-(carbamoyl)phenyl diselenides (**2**) since their utility as oxygen-transfer catalysts and biological response modifiers [5–10]. In our previous works we reported synthesis of some related compounds 1,3,2-benzothiaselenazole 1,1-dioxides (**3**) and 2,2′-diselenobis(benzenosulfonamides) (**4**) [11,12] (Scheme 1).

Expecting that replacement of the carbonyl group in parent compounds **1** and **2** by a sulfonyl group should result in enhancement of biological response and catalytic activity in oxygen transfer processes, in this work we have undertaken a more detailed study on the chemistry and biology of the mentioned above compounds **3** and **4**.

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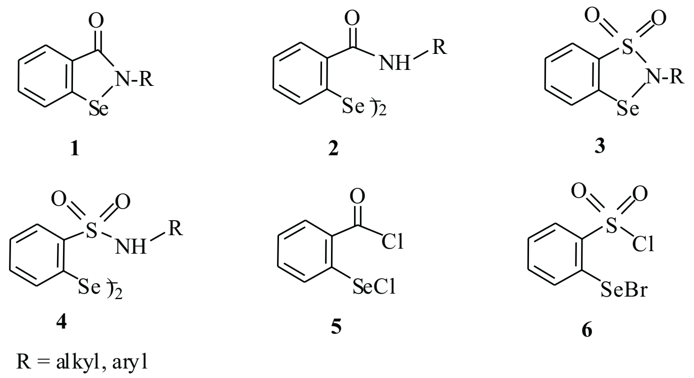
Scheme 1



1 2 3

4 5 6

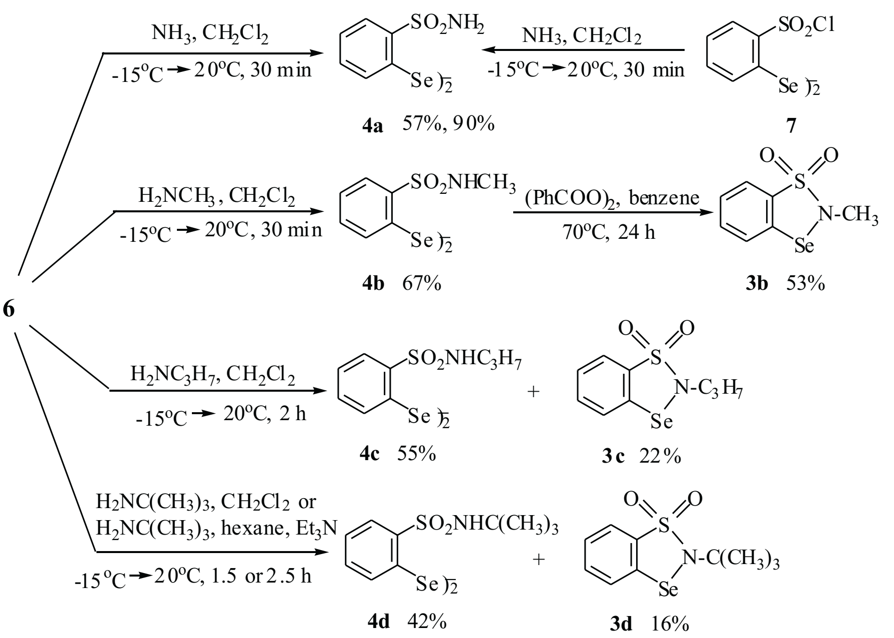
R = alkyl, aryl

It has been known, that 2-(chloroseleno)benzoyl chloride **5** reacting with various N, O and S nucleophiles acted as selenylating, acylating or tandemic selenenylating-acylating agent and different products depending on substrate used and reaction conditions were produced [11]. Since its analog 2-(chloroseleno)benzenesulfonyl chloride was unstable and easily decomposed, in this work 2-(bromoseleno)benzenesulfonyl chloride (**6**) was used as a key substrate. This particular compound has two different electophilic centers. One of them (hard electrophilic center is localized on the sulfonyl sulfur atom and the second one (soft electrophilic center) is the selenium atom. Since both of these centers may compete toward nucleophiles, such as primary amines, the sulfonamides, selenenamides as well as cyclic products, having both of these groups in the ring, could be expected as the reaction products.

RESULTS AND DISCUSSION

First group of the nucleophiles employed in this work were ammonia, methyl-, *n*-propyl- and *t*-butylamine. The molar ratio of the primary amine to the substrate **6** was from 1:1 to 4.4:1, dependent on the nature of amine, and reaction was carried out in the conditions given in Scheme 2. When ammonia in exces was a reagent, 2,2′-diselenobisbenzenesulfonamide (**4a**) was a product. The same compound was obtained by sulfonylation of ammonia with bis[2-(chlorosulfonyl)] diselenide (**7**). The reaction of **6** with methylamine gave 2,2′-diselenobis(N-methylbenzenesulfonamide) (**4b**), while the similar reaction with *n*-propylamine and *t*-butylamine led to the mixtures of 2,2′-diselenobis(benzenesulfonamides) **4c** and **4d** and corresponding 1,3,2-benzothiaselenazole 1,1-dioxides **3c** and **3d** being the products of tandem sulfonylation-selenenylation of the primary amino group. In the additional experiment for *t*-butylamine was used in stoichiometric amount (1 mol) and triethylamine was taken as a base for binding of eliminated hydrogen halides. The result was the same as mentioned above and both compounds **3d** and **4d** were produced. It should be noted that formation of cyclic products **3** were not observed, when ammonia and methylamine were the reagents. 2-Methyl-1,3,2-benzothiaselenazole 1,1-dioxide (**3b**) was obtained in usual way [12] by oxidative cyclization of diselenide **4b**.

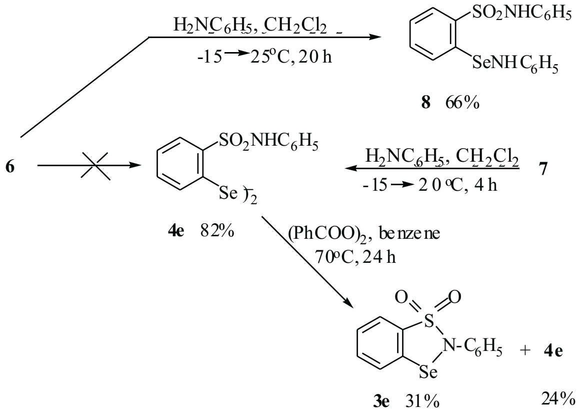
Scheme 2



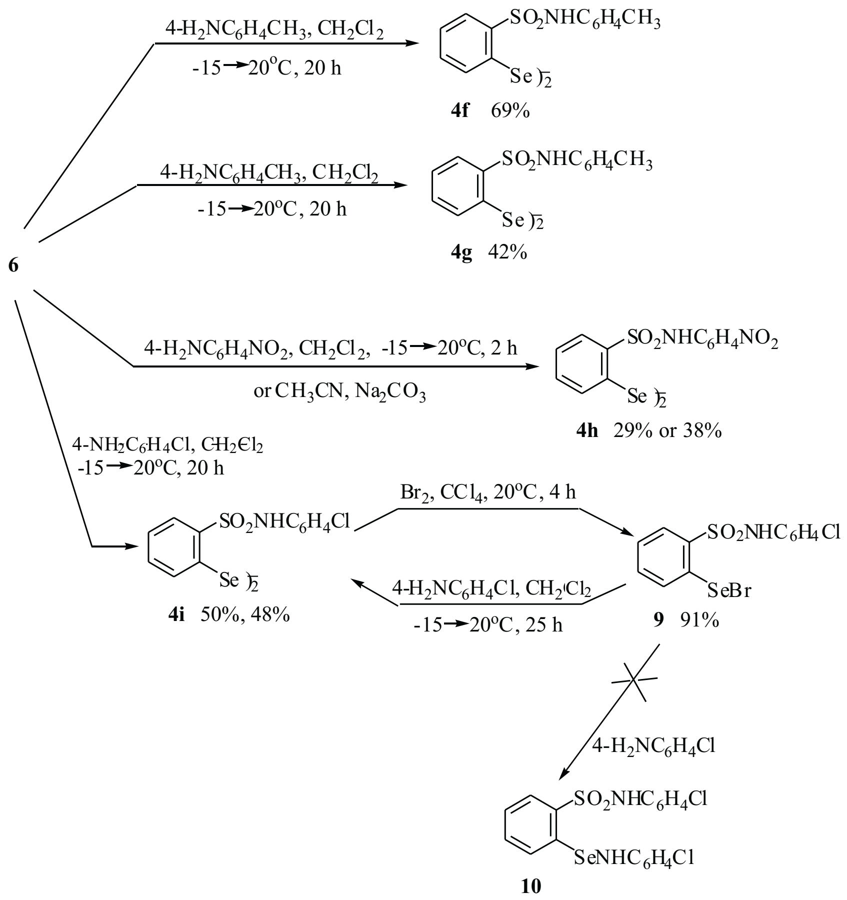
On the contrary, the reaction of 2-(bromoseleno)benzenesulfonyl chloride (**6**) with aniline led to 2-(sulfamoylphenyl)phenylselenenylanilide (**8**), while neither expected diselenide **4e** nor 2-phenyl-1,3,2-benzothiaselenazole 1,1-dioxide (**3e**) were found in the reaction mixture. The compound **4e** was obtained on another way, by treatment of bis[2-(chlorosulfonyl)] diselenide (**7**) with aniline. In the nex step it was oxidized with benzoyl peroxide to cyclic sulfonamide **3e** (Scheme 3).

The reaction of chlorobromide **6** with anilines substituted in *para*-position of the benzene ring with electron-donating (CH_3, OCH_3) as well as with electron-withdrawing (NO_2, Cl) groups resulted in formation of corresponding diselenides **4f–i** as shown in Scheme 4. We attempted to obtain the compound **10**, being an analog of 2-(sulfamoylphenyl)phenylselenenylanilide (**8**), by selenenylation of 4-chloroaniline with 2-(bromoseleno)-N-(4-chlorophenyl)benzenesulfonamide (**9**) but diselenide **4i** instead of expected compound **10** was obtained.

Scheme 3

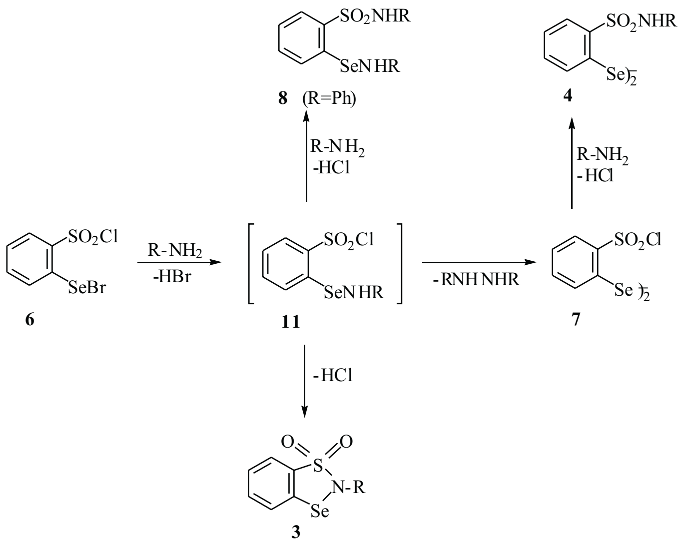


Scheme 4



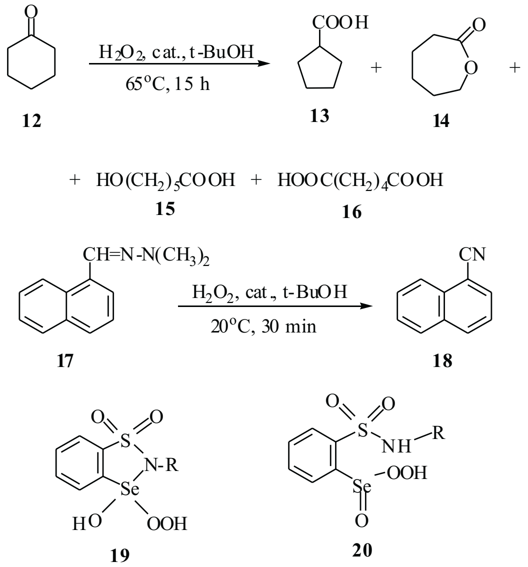
The results presented in this work suggest, that the compounds having selenenamide moiety, like to other noncyclic selenenamides, are generally unstable and that compound **8** is an only exception. Most probably bromoseleno group in chlorobromide **6**, more reactive than chlorosulfonyl group, acts as selenenylating agent and selenenamide **11** is formed in the first step of the reaction. Two molecules of **11** disproportionate producing diselenide **7**, similarly as it was observed earlier for the compounds having hydroxy, cyano, or sulfide group or halogen on the selenium atom [1,13]. In the next step amine, sulfonylated by chlorosulfonyl group of **7**, give 2,2′-diselenobis(benzenesulfonamide) (**4**). When aniline is a reagent, selenenamide **11** reacts with second molecule of amine and stable compound **8** is a final product. Moreover, selenenamide **11** can undergo intramolecular sulfonylation, resulted in formation of N-substituted 1,3,2-benzothiaselenazole 1,1-dioxides (**3**) (Scheme 5). The latter reaction is similar to reported earlier cyclization of 2-(bromoseleno)-N-*tert*-butylbenzenesulfonamide [12].

Scheme 5



The compounds **3** and **4** were tested as oxygen-transfer catalyst for hydrogen peroxide and *t*-butylhydroperoxide oxidation of cycloalkanones and N,N-dimethylhydrazones (Scheme 6). In our earlier work we reported a conversion of cycloalkanones into cycloalkanecarboxylic acids with hydrogen peroxide, an organoselenium catalyst. Among them poly(bis-9,10-anthacenyl)diselenide (PADS) was found as a most efficient catalyst. Produced cycloalkanecarboxylic acids were accompanied by other products of the oxidation thus as lactones, hydroxy- and dicarboxylic acids [14]. In the work presented here, the model substrate was cyclohexanone **12**, which produced a mixture of cyclopentane carboxylic acid (**13**), lactone **14**, 5-hydroxypentanecar-

Scheme 6



boxylic- and adipic acid (**15** and **16**). The catalyst was used in 0.06 mol % and the oxidant was 30% aqueous hydrogen peroxide or 80% *t*-butyl hydroperoxide and the reaction was carried out in *t*-butanol at 65°C for 15 h. The results, presented in Table 1, show that majority of tested compounds exhibited a catalytic activity similar to ebselen. The exception was diselenide **4d**, which induced high conversion of the substrate and ring cleavage to acids **15** and **16**. Nevertheless, the compounds **1**, (R = Ph), **3** and **4** were less active than PADS. When *t*-butyl hydroperoxide was taken as an oxidant instead of hydrogen peroxide, the conversion of **12** to products **13–16** was lower. Most probably the compounds **3** act *via* active intermediates hydroperoxyselenuranes **19**, while diselenides **4** *via* peroxyareneseleninic acid **20** in the similar way as it was reported earlier for their carbonyl analogues **1** and **2** [5,8].

The selenium compounds, listed in Table 1, were also tested as catalysts for hydrogen peroxide oxidation of N,N-dimethylhydrazone 1-formylnaphthalene (**17**) to nitrile in the manner as presented in Scheme 6. Generally, oxidative conversion of N,N-methylhydrazones to nitriles is a well known reaction and ebselen and PADS (used in 5 mol %) is known as a one of the most effective catalyst [7,15]. Using in this work catalyst only in 0.1 mol %, we find that compound **3e**, being a sulfonyl analog of ebselen **1**, (R = Ph) was more active than other tested compounds (among them ebselen) since afer 30 min the subtrate **17** was converted in nitrile **18** in 40%, while conversion of the same compound for other catalyst was in the range 2–13%. Moreover, when oxidation was carried out for longer time (5 hrs) the 1-cyanonaphthalene **18** was obtained in 98% yield.

Table 1. Hydrogen peroxide oxidation of cyclohexanone catalyzed by organoselenium compounds.

Catalyst	Unreacted substrate[a] **12**, %	Products[a] (**13** + **14**) %	(**15** + **16**) %
none	98	0	0
1	54	15	31
3b	36	21	43
3c	58	18	24
3d	55	15	30
3e	60	18	22
4b	35	18	47
4c	32	12	56
4d	12	8	75
4e	56	20	36
PADS[b]	0	60	40

[a] Determined by GC. [b] Reaction time 3.5 h.

The ebselen (**1**, R = Ph) and **3b–e**, **4b–e**, **4h** and **8** were tested against gram-positive (*S. aureus, B. subtilis*) and gram-negative (*E. coli*, *P. putida*) bacterial strains *in vitro*. In contrast to ebselen [16] other compounds were inactive (MIC > 512 μg/ml) except **4e**, which was moderately active against usually resistant sporulating rods (MIC = 64 μg/ml). The antifungal tests against *C. albicans, A. niger and P. citrinum* gave negative results.

Cytotoxicity of the same compounds was determined in human lung adenocarcinoma cell line A549 (ATCC 185) and antiviral against VSV (vesicular stomatitis virus, *Rhabdoviridae*, enveloped virus), EMCV (encephalomyocarditis virus, *Picornaviridae*, naked virus) and HSV-1 (herpes simplex virus type 1, *Herpesviridae*, enveloped virus) were measured *in vitro* and compared with activity of reference ebselen. All of the tested compounds were inactive against VSV or its activity (ebselen, **3e**) was low (MIC > 600 μg/ml). The high activity against HSV-1 and EMCV was observed for ebselen, sulfonamide **4b** and 1,3,2-benzothiaselenazole 1,1-dioxides **3b** and **3c** (Table 2). It should be noted high Index values for ebselen and **4b**, which qualified them to more advanced biological investigations. Other tested compounds were inactive against both of these viruses.

CONCLUSIONS

In this work we show that 2-(bromoseleno)benzenosulfonyl chloride (**6**), having two different electrophilic centers localized on the sulfur and selenium atom, treated with ammonia, primary aliphatic or aromatic amines gives 2,2′-diselenobis(benzenesulfonamides) **4** accompanied in some cases by 1,3,2-benzothiaselenazole 1,1-

dioxides (**3**) being the products of tandem sulfonylation-selenenylation of amino group. Exceptionally, when aniline is a reagent, 2-(sulfamoylphenyl)phenylselenenylanilide (**8**) was produced. These results are different from these, when analogue of **6** 2-(chloroseleno)benzoyl chloride (**5**) is an substrate and tandem acylation-selenenylation lead to the ring formation and N-substituted benzisoselenazol-3(2H)-ones are produced exclusively [12,17]. Most probably bromoseleno group in the substrate **6**, more reactive than chlorosulfonyl group, acts in the first step of the reaction as selenenylating agent and selenenamide **11** is formed as an active intermediate, which quickly undergoes subsequent reactions.

Table 2. Cytotoxicity and antiviral activity of selected selenium compounds.

Compounds	Cytotoxicity μg/ml	HSV-1		EMCV	
		MIC[a]	Index[b]	MIC[a]	Index[b]
ebselen	15	2.0	7.5	10	1.5
3b	7.5	20	0.375	20	0.375
3c	15	60	0.250	20	0.750
4b	15	4.0	3.75	4	3.75

[a]Minimal inhibiting virus concentration (μg/ml), [b]Index = Cytotoxicity/MIC.

The test of the compounds **3** and **4** as oxygen-transfer transfer agents for hydrogen peroxide oxidation of cyclohexanone to acids and 1-naphthaldehyde N,N-dimethylhydrazone to the nitrile exhibited their appreciable catalytical activity similar or even higher than activity of ebselen.

Antifungal and antibacterial tests have shown, that compounds **3** and **4** are inactive or their activity is substantially lower than activity of reference ebselen. For sulfonamide **4b** and 1,3,2-benzothiaselenazole 1,1-dioxides **3b** and **3c** high activity against viruses HSV-1 and EMCV was observed.

EXPERIMENTAL

Melting points: Digital Melting Point Apparatus Electrothermal IA 9100. ^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker DRX 300 (300 MHz) spectrometer. Chemical shifts (δ) are reported in ppm with Me_4Si as internal standard. IR (KBr pellets or CCl_4); Perkin-Elmer 2000 FT. All starting materials were purchased from Aldrich Chem. Co. and Fluka. Dichloromethane, acetonitrile, benzene and hexane were distilled from P_2O_5 before using. Triethylamine, *n*-propylamine, *tert*-butylamine and pyridine were freshly distilled from NaOH. 2-Phenyl-1,3,2-benzothiaselenazole 1,1-dioxides (**3e**), 2,2′-diselenobisbenzenesulfonamides **4e**, **4i**, 2-(bromoseleno)benzenesulfonyl chloride (**6**) and 2-(bromoseleno)benzenesulfonamide (**9**) were obtained from bis(2-chlorosulfonylphenyl) diselenide following the ways reported in ref. [11,12]. 1-Naphthaldehyde N,N-dimethylhydrazone **17** was prepared by treating of 1-naphthaldehyde with N,N-dimethylhydrazine in methanol according to procedure reported in ref. [18]. Ebselen was synthesized from anthranilic acid [17] and poly(bis-9,10-anthracenyl)diselenide (PADS) by selenenylation of 9,10-dibromoanthracene [14].

The antimicrobial activities of tested compounds were evaluated by the agar dilution method [19]. Nutrient Agar and Mycological Agar were used for bacteria and fungi respectively. Gram-positive bacterial species; *Staphylococcus aureus* PCM 1944, *Bacillus subtilis* PCM 1949. Gram-negative bacteria species; *Escherichia coli* PCM 2057 and *Pseudomonas putida* PCM 2124. Fungal strains; *Candida albicans*, *Aspergillus niger* and *Penicillium citrinum* were used for the test.

Cytotoxicity of the compounds was determined in human lung adenocarcinoma cell line A549 (ATCC 185). The experimental was performed in 96-cells microplates. The cells were treated with various doses of the compounds for 48 h at 37°C in the atmosphere of 5% CO_2 in air. Then the cultures were examined under microscope and stained with MTT. The minimal concentration, which was toxic to approximately 50% of the cells, was taken as $TCCD_{50}$ [20].

The compounds in various concentrations incubated with following viruses: EMCV (encephalomyocarditis virus, *Picornaviridae*, naked virus), HSV-1 (herpes simplex virus type 1, *Herpesviridae*, enveloped virus) and VSV (vesicular stomatis virus, *Phabdoviridae*, enveloped virus). Viruses VSV and EMCV were used at 10^5 $TCID_{50}$/ml. After 2 h inhibiting concentration at r.t. the virus titer was measured in human A549 cells and minimal virus-inhibiting concentration (MIC) was determined.

Synthesis of 2,2′-diselenobisbenzenesulfonamides 4a–b: A vigorously stirred cooled on ice/salt bath solution of 2-(bromoseleno)benzenesulfonyl chloride (**6**) (0.502 g, 1.5 mmol) in dry methylene chloride (50 ml) was saturated by dry ammonia or methylamine over 30 min respectively. After 1 h, during which the mixture was allowed to warm to room temperature, the solvent and excess of ammonia or amine were removed *in vacuo*. From the residue amine hydrohalide was washed off by stirring with water overnight and product **4a–4b** was filtered off, washed with water and dried by air. Compound **4b** was recrystallized from methanol (100 ml).

2,2′-Diselenebis(benzenesulfonamide) (4a): Pale yellow powder; yield 0.202 g (57%), m.p. 243–254°C (decomposed), ref. [12] 253–255°C.

2,2′-Diselenobis(N-methylbenzenesulfonamide) (4b): Yellow prisms. Yield: 0.501 g (67%), m.p. 184–185°C, ref. [11] 185–187°C.

2-Methyl-1,3,2-benzothiaselenazole 1,1-dioxide (3b): A mixture of the diselenide **4b** (0.498 g, 1.0 mmol), benzoyl peroxide (0.266 g, 1.1 mmol) and dry benzene (25 ml) was stirred and heated at 70°C for 24 h. After the reaction had finished, benzene was evaporated *in vacuo* and the residue were separated by silica gel chromatography (dichloromethane) to give **3b** (0.262 g) as white needles. Yield: 0.262 g (53%), m.p. 102–104°C (carbon tetrachloride), ref. [11] 98–100°C.

Reaction of 2-(bromoseleno)benzenesulfonylchloride (6) with *n*-propylamine: A solution of compound **6** (0.502 g, 1.5 mmol) in dry dichloromethane (20 ml) was added dropwise for 30 minutes to a stirred and cooled (ice/salt bath) solution of propylamine (0.390 g, 6.6 mmol) in dry dichloromethane (10 ml). After additional 2 h the solvent was evaporated *in vacuo* and from the residue 2-propyl-1,3,2-benzothiaselenazole 1,1-dioxide (**3c**) was isolated on the silica gel column (dichloromethane) as a first fraction. White needles, yield 0.090 g (22%), m.p. 85–86°C, ref. [12] 84–86°C. The next fraction contained **4c**: Yellow prisms. Yield: 0.228 g (55%), m.p. 130–131°C, ref. [12] 130–132°C.

Reaction of 2-(bromoseleno)benzenesulfonylchloride (6) with *t*-butylamine: A solution of compound **6** (0.502 g, 1.5 mmol) in dry hexane (20 ml) was added dropwise over 1 h to a stirred and cooled (ice/salt bath) solution of *t*-butylamine (0.16 ml, 0.110 g, 1.5 mmol) and triethylamine (0.85 ml, 0.607 g, 6.0 mmol) in dry hexane (10 ml). After additional 2.5 h the reaction mixture was worked up as in the reaction with *n*-propylamine. From the residue **3d** was isolated by column chromatography as a first fraction and **4d** as a second fraction. **3d**: Colourless needles. Yield: 0.069 g (16%), m.p. 129–130°C, ref. [12] 112.5–115°C **4d**: Yellow prisms. Yield 0.182 g (42%), m.p. 209–211°C, ref. [12] 208–209°C.

Reaction of 2-(bromoseleno)benzenesulfonylchloride (6) with aniline: To a vigorously stirred, cooled on ice/salt bath solution of aniline (1.27 ml, 1.30 g, 13.2 mmol) in dry dichloromethane (25 ml) the solution of 2-(bromoseleno)benzenesulfonylchloride (**6**) (1.004 g, 3.0 mmol) in dry dichloromethane (20 ml) was dropped over 40 min. The reaction was continued for additional 20 h, while the mixture warmed to room temperature, solid was filtered of, extracted with dichloromethane and from the combined filtrates solvents were evaporated *in vacuo*. Hydrochloric acid (5% in water) was added to the residue, the mixture was stirred for 3 h and the precipitate solid was filtered off, washed with water, dried in air and purified by column chromatography (silica gel, dichloromethane) to give 2-(sulfamoylphenyl)phenylselenenylaniline (**8**). Yield 0.819 g (66%), m.p. 170–174°C (dichloromethane – hexane, 2:1), IR (KBr): γ = 3429 and 3354 cm^{-1} (NH), 1338 and 1159 cm^{-1} (SO_2). ^{1}H NMR ($CDCl_3$): 7.78 (d, J = 8.1 Hz, 1H, ArH); 7.54 (s, 1H, ArH); 7.40 (d, J = 8.1 Hz, 2H, ArH); 7.21 (d, J = 7.6 Hz, 2H, ArH); 7.17–7.13 (m, 6H, ArH); 6.69 (d, J = 8.1 Hz, 2H, ArH); 3.90 (s, 2H, NH). Anal. calcd. for $C_{18}H_{16}N_2O_2SeS$ (403.36): C, 53.60; H, 4.00; N, 6.95. Found: C, 53.50; H, 4.07; N, 6.71.

Diselenide 4f and 4g: A solution of compounds **6** (0.502 g, 1.5 mmol) in dry dichloromethane (20–25 ml) was added dropwise over 0.5–1 h to a stirred and colled (ice/salt bath) solution of 4-methyl- or 4-methoxyaniline (6.6 mmol) in dry dichloromethane (20 ml). The reaction was continued for additional 20 h, while the mixture warmed to a room temperature. Reaction mixture was washed with 5% hydrochloric acid, dried with anhydrous sodium sulfate, solvent was distilled of *in vacuo* and product purified by column chromatography (silica gel, dichloromethane).

2,2′-Diselenobis[N-(4-methylphenyl)benzenesulfonamide] (4f); yellow prisms, yield 0.336 g (69%), m.p. 174–176°C, ref. [12] 175–177°C.

2,2′-Diselenobis[N-(4-methoxyphenyl)benzenesulfonamide] (4g); yellow prisms, yield 0.215 g (42%), m.p. 183–185°C (decomposition) (ref. [12] 183–185°C).

Reaction of chlorobromide 6 with 4-nitroaniline: A solution of chlorobromide **6** (0.502 g, 1.5 mmol) in dry acetonitrile (15 ml) was added dropwise over 40 minutes to a stirred and cooled (ice/salt bath) mixture of 4-nitroaniline (0.207 g, 1.5 mmol) and K_2CO_3 (2.07 g, 1.5 mmol) in dry acetonitrile (25 ml). After additional 2.5 h the reaction mixture was stored in refrigerator by night and then the solid was filtered up. From filtrate solvent was evaporated *in vacuo* and crude 2,2′-diselenobis[N-(4-nitrophenyl)benzenesulfonamide] (**4h**) was purified by column chromatography (silica gel, dichloromethane). Yellow prisms, yield 0.191 g (38%), m.p. 244–245°C (decomposition). IR (KBr): γ = 3242 cm^{-1} (NH), 1518 cm^{-1} (NO_2), 1343 cm^{-1} (NO_2 and SO_2), 1162 cm^{-1} (SO_2). ^{1}H NMR (DMSO-d$_6$): 11.77 (s, 2H, NH), 8.17 (d, J = 9.0 Hz, 4H, ArH); 8.01 (d, J = 7.7 Hz, 2H, ArH); 7.75 (d, J = 7.7 Hz, 2H, ArH); 7.47 (dd, J = 7.7 Hz, 2H, ArH); 7.39 (dd, J = 7.7 Hz, 2H, ArH); 7.34 (d, J = 9.0 Hz, 4H, ArH). Anal. calcd. for $C_{24}H_{18}N_4O_8Se_2S_2$ (712.47): C, 40.46; H, 2.55; N, 7.86. Found: C, 40.50; H, 2.40; N, 7.61.

Reaction of chlorobromide 6 with 4-chloroaniline: A solution of chlorobromide **6** (0.502 g, 1.5 mmol) in dry dichloromethane (20 ml) was added dropwise over 30 minutes to a stirred and cooled (ice/salt bath) mixture of 4-chloroaniline (0.383 g, 3.0 mmol) in dry dichloromethane (20 ml). After additional 1 h, from cooled reaction mixture solid was filtered up, and solvent was evaporated *in vacuo*. To red solid residue pyridine (10 ml) was added and mixed in room temperature overnight. A solvent was distilled of *in vacuo*, dichloromethane was added (100 ml), washed with 5% hydrochloric acid (50 ml) and water (50 ml), dried with anhydrous sodium sulfate and dichloromethane was distilled of *in vacuo* and 2,2′-diselenobis[N-(4-chlorophenyl)benzenesulfonamide] (**4i**) was purified by column chromatography (silica gel, dichloromethane). Yellow needles. Yield: 0.261 g (50%), m.p. 185–188°C (decomposition), ref. [12] 184–186°C.

Reaction of 2-(bromoseleno)-N-(4-chlorophenyl)-benzenesulfonamide (9) with 4-chloroaniline: A solution of selenobromide **9** (0.426 g, 1.0 mmol) in dry dichloromethane (20 ml) was added dropwise other 30 minutes to a stirred and cooled (ice/salt bath) solution of 4-chloroaniline (0.268 g, 2.1 mmol) in dry dichloromethane (10 ml). After additional 2 h reaction mixture was colled in refrigerator and formed suspension was filtered up. Filtrate was washed with hydrochloric acid (2×25 ml), water (25 ml), dried by Na_2SO_4 and solvent was distilled *in vacuo*. 2,2′-Diselenobis[N-(4-chlorophenyl)benzenesulfonamide] (**4i**) was purified by column chromatography (silica gel, dichloromethane), yield 0.167 g (48%), m.p. 185–188°C (decomposition), ref. [12] 184–186°C.

Hydroperoxide oxidation of cyclohexanone 12: Aqueous hydrogen peroxide (30%, 1.63 ml, 16 mmol) or *t*-butylhydroperoxide (TBHP) (80%, 2.0 ml, 16 mmol) was added to a stirred and heated to 65°C mixture of cyclohexanone (0.83 ml, 8.0 mmol) an selected catalyst **1**, **3b–e**, **4b–e**, **PADS** (5 μmol, 0.06 mol %) in *t*-butanol (1.5 ml). After additional 15 h reaction mixture was cooled to room temperature and analysed by GC.

Hydrogen peroxide oxidation of N,N-dimethylhydrazone-1-naphthaldehyde (17) into 1-cyanonaphthalene (18): Aqueous hydrogen peroxide (30%; 5.0 ml, 50 mmol) was added to a stirred solution of dimethylhydrazone **17** (1.983 g, 10 mmol) and the catalyst **1**, **3b–e**, **4b–e**, **PADS** (10 μmol, 0.10 mol %) in *t*-butanol (60 ml), and the mixture was stirred at 65 °C for 30 min. After this period, the reaction mixture was poured into aqueous saturated sodium carbonate (2.5%) and sodium chloride (7.5%)

(50 ml) and extracted with chloroform (30 ml + 4 × 15 ml), dried other anhydrous sodium sulfate and filtered. The solvent was evaporated *in vacuo* and the residue was analysed by means of ^{1}H NMR.
The reaction was carried out in the same way in a preparative scale using 2-phenyl-1,3,2-benzothiaselenazole 1,1-dioxide (**3e**) (3.10 mg 10 mmol) as a catalyst. Reaction is prolonged for 5 hrs. The residue after filtration by short silica gel column (dichloromethane) was essentially pure 1-cyanonaphthalene (**18**); 1.50 g, 9.79 mmol (98%), m.p. 38–39°C (hexane), ref. [7] m.p. 37–39°C. ^{1}H NMR ($CDCl_3$); 8.22 (d, J = 8.5 Hz, 1H, ArH); 8.03 (d, J = 8.3 Hz, 1H, ArH); 7.86 (m, 2H, ArH); 7.67 (ddd, J = 8.4, 7.0, 1.3 Hz, 1H, ArH); 7.58 (ddd, J = 8.6, 7.0, 1.1 Hz, 1H, ArH); 7.49 (dd, J = 8.3, 7.2 Hz, 1H, ArH).

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