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LITHIUM DISELENIDE IN APROTIC MEDIUM - A CONVENIENT REAGENT FOR SYNTHESIS OF ORGANIC DISELENIDES

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Abstract - The reduction of selenium with lithium in THF in the presence of diphenylacetylene as a catalyst afforded lithium diselenide, which reacted with electrophiles giving alkyl or aryl diselenides 1 - 3 and selenides 4, as by-products. The useful method for preparation of diselenides based on this reaction was elaborated.

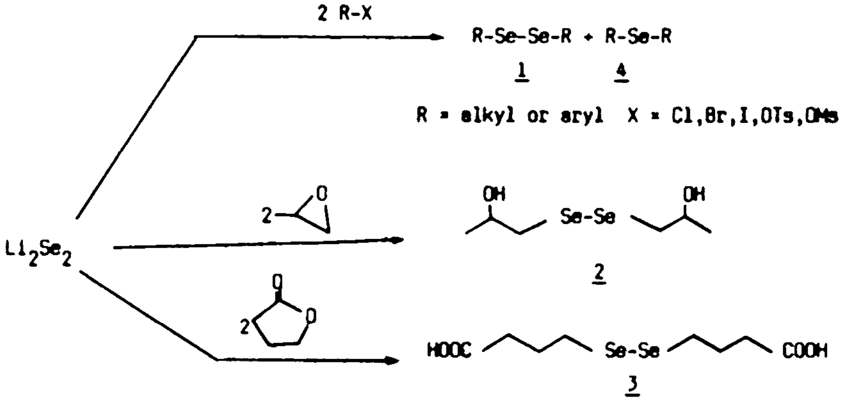
The chemistry of organoselenium compounds, due to their usefulness as the reagents in organic synthesis, is actually extensively developing[1-4]. In our recent works a number of organoselenium compounds was reported, among them arylperoxyseleninic acids, the effective oxidants, and bis(2-nitrophenyl) or bis(2,4-dinitrophenyl) diselenides - activators of hydrogen peroxide useful as catalysts in the Baeyer-Villiger oxidation of aromatic and α,β-unsaturated aldehydes[5-8]. On the other hand, the existing methods of preparation of organoselenium compounds, especially of organic diselenides, are troublesome and expensive as a rule[9-19].

The investigations presented in this paper concern synthesis of diaryl or dialkyl diselenides being important substrates for preparation of various organoselenium compounds. The most frequently used method for preparation of organic diselenides is reaction of alkali metal diselenides with various electrophiles. One could suppose that lithium diselenide in aprotic solvent should be more convenient reagent for preparation of organic diselenides than other alkali metal diselenides in prototropic solvents. Lithium diselenide is appreciably soluble in THF and amidic solvents (DMF, HMPT etc.). The known method for preparation of lithium diselenide in THF consists in reduction of selenium with lithium triethylborohydride[20]. Nevertheless, this method is expensive and the product is accompanied by triethylborane. Now we elaborated more convenient method based on the catalytic reduction of selenium with lithium in THF. The reaction between lithium and selenium is thermodynamically allowed but it does not take place because of their unsolubility in aprotic medium. Therefore we searched for catalysts of this reaction and found that lithium and selenium react smoothly at room temperature in the presence of small amount (ca 3 mol %) of diphenylacetylene. The reagents should be used in stoichiometric amounts because the reaction does not stop on the diselenide step, when lithium was used in excess, lithium selenide was formed. The method elaborated permits to obtain lithium diselenide in very cheap and convenient way.

$$2Se + 2Li \xrightarrow[\text{THF, } 20^{\circ}C]{\text{cat. } C_6H_5C\equiv CC_6H_5} Li_2Se_2$$

The reaction involves electron transfer from lithium to selenium. Although diphenylacetylene was not detected among the reaction products, it is reasonable to suppose that this compound or its derivatives act as electron carriers.

Lithium diselenide easily interact with carbon electrophiles. Substitution of the halogen atoms, mesyl or tosyl groups took place and diselenides 1 - 3 were formed, although in some cases aromatic and heteroaromatic diselenides 1 were accompanied by selenides 4 being the minor products. In the case of aliphatic substrates, no selenide formation was observed.



The electrophilic carbon atoms of the oxirane or lactone ring were also attacked by the diselenide anion, and ring opening led to corresponding diselenides 2 or 3. In most cases the reaction proceeded at room temperature in THF. When electrophile was less reactive the reaction had to be carried out at higher temperature and HMPT or HMPT and THF was used as a solvent. The reaction conditions, results obtained and physicochemical data of the products 1 - 4 are given in Table 1. The spectroscopic data of new diselenides 1 - 3 and selenides 4, 6 are listed in Table 2.

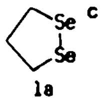
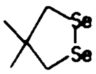
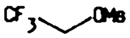
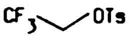
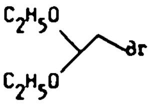
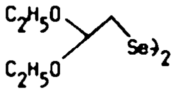
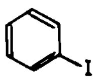
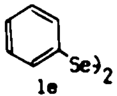
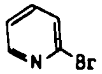
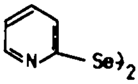
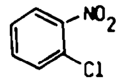
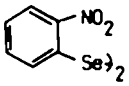
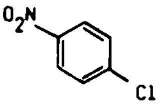
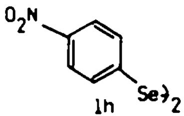
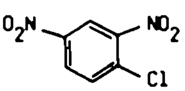
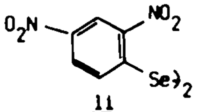
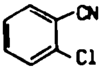
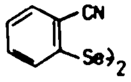
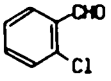
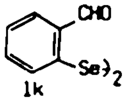
In the other experiments with reaction of lithium diselenide with trimethylchlorosilane, only bis(trimethylsilyl) selenide 5 was obtained instead of expected bis(trimethylsilyl) diselenide. The same compound 5 was obtained when lithium selenide was used as a reagent.

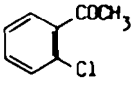
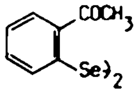
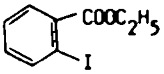
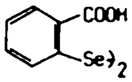
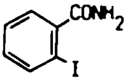
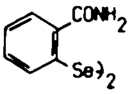
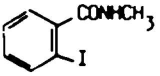
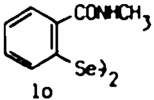
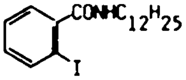
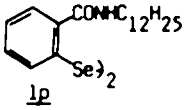
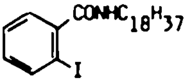
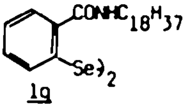
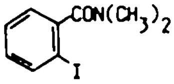
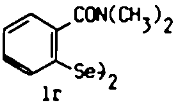
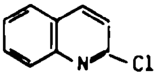
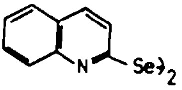
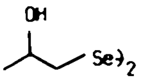
$$2(CH_3)_3SiCl \xrightarrow{Li_2Se_2,\ THF,\ -80^oC} (CH_3)_3SiSeSi(CH_3)_3 + LiCl + Se$$

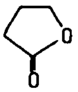
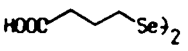
5

It is interesting that lithium diselenide reacts with trimethylchlorosilane very fast at -80°C, whereas the reaction with lithium selenide is very slow even at 20°C. It should be mentioned that, as described in the literature[21], lithium selenide efficiently reacts with trimethylchlorosilane at room temperature. In our experiments refluxing was necessary. Addition of small amount of boron trifluoride etherate (1.6 mol %) accelerated substantially the reaction, thus the differences observed should be ascribed to the presence of triethylborate in the solution of lithium selenide obtained by Detty and Seidler[21].

Table 1. Results of Reaction of Lithium Diselenide with Various Electrophiles

Electrophile	Reaction conditions (solvent, temperature, time)	Products				
		Diselenide			Other	
		Formula[a]	Yield[b] [%]	m.p.(solvent) or b.p./torr [°C]	Compound[a]	Yield [%][b]
	THF, 20°C, 0.5 h	 c 1a	98	65-70[d] lit[22] above 60	-	-
	THF, 20°C, 20 min		96		-	-
	THF, 20°C, 0.5 h 67°C, 2 h	 1b	76	m.p. 37 (hexane) b.p. 118/15 lit[15] m.p.34-35		
	THF, 20°C, 0.5 h 67°C, 2 h		87			
	THF, 20°C, 0.5 h	 1c	59	b.p. 161/76	-	-
	THF, 20°C, 0.5 h 67°C, 1 h		64		-	-
	THF, 20°C, 0.5 h 67°C, 1 h		52		-	-
	THF, 20°C, 5 h	 1d	81	b.p. 137/0.15	-	-
	HMPT,115-120°C, 22 h 140-150°C, 28 h	 1e	71	m.p. 63 (EtOH) Lit[23] 63	-	-
	THF/HMPT, 20°C, 24 h 115-120°C, 4 h	 1f	54	m.p. 50 (i-Pr$_2$O/AcOEt) lit[24] 48-49	4f[e]	14
	THF/HMPT, 20°C, 20 h	 1g	86	m.p. 220 (PhCl) lit[13] 212-213	-	-
	THF, 20°C, 24 h	 1h	83	m.p. 180 (PhCl) lit[18] 179-180	-	-
	THF, 5°C, 0.5 h	 1i	97	decomp. 263 (DMF) lit[10] 264-265	-	-
	HMPT, 115-120°C, 6 h	 1j	38	m.p. 115 (CHCl$_3$/CCl$_4$)	4j[e]	23
	THF/HMPT, 20°C, 18 h 115-120°C, 6 h	 1k	37	m.p. 172 (CHCl$_3$/AcOEt)	4k[e]	6

Electrophile	Reaction conditions (solvent, temperature, time)	Products				
		Diselenide			Other	
		Formula[a]	Yield[b] [%]	m.p.(solvent) or b.p./torr [°C]	Compound[a]	Yield [%][b]
	THF/HMPT, 20°C, 18 h 115-120°C, 7 h	 1l	27	m.p. 192 (cyklohexane benzene)	4l[e] 6[f]	3.5 24
	HMPT, 115-120°C, 26 h	 1m	28	decomp. 297 (AcOH/dioxane) lit[16] 296-297	-	-
	HMPT, 115-120°C, 19 h	 1n	70	decomp. 269 (dioxane) lit[16] 265-266	-	-
	HMPT, 115-120°C, 23 h	 1o	58	m.p. 263 (AcOH/DMF)	-	-
	HMPT, 115-120°C, 25 h	 1p	45	m.p. 127 (AcOEt)	4p[e]	5.0
	HMPT, 115-120°C, 26 h	 1q	52	m.p. 125 (AcOEt)	4q[e]	7.4
	HMPT, 115-120°C, 24 h	 1r	47	m.p. 166 (dioxane)	4r[e]	10.0
	HMPT, 115-120°C, 4 h	 1s	57	m.p. 147 (dioxane/AcOEt)	4s[e]	23
$C_2H_5OCOCH_2Cl$	THF, 5°C, 20 min	$C_2H_5OCOCH_2Se)_2$ 1t	78	b.p. 120/0.1	-	-
$C_2H_5OCOCH_2CH_2Br$	THF, 5°C, 20 min	$C_2H_5OCOCH_2CH_2Se)_2$ 1u	94	b.p. 142/0.1	-	-
$(C_2H_5)_2NCH_2CH_2Cl$	THF, 20°C, 2 h 67°C, 0.5 h	$(C_2H_5)_2NCH_2CH_2Se)_2$ 1w	83	b.p.124/0.13	-	-
$(C_6H_5)_2CHCl$	THF, 20°C, 3 h 67°C, 0.5 h	$(C_6H_5)_2CHSe)_2$ 1x	84	m.p. 126 (hexane)	-	-
	THF, 20°C, 0.5 h	 2	93	b.p.133/0.20	-	-

Electrophile	Reaction conditions (solvent, temperature, time)	Products				
		Diselenide			Other	
		Formula[a]	Yield[b] [%]	m.p.(solvent) or b.p./torr [°C]	Compound[a]	Yield [%][b]
	THF, 20°C, 1 h 67°C, 10 min		82	m.p. 74 (i-Pr$_2$O/AcOEt)	-	-
$(CH_3)_3SiCl$	THF, -80°C, 10 min THF, -10°C, 10 min	- -	- -	- -	5[e]	73[g] 69[g]

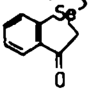
[a] Satisfactory microanalyses obtained: C ± 0.4%, H ± 0.3%, Se ± 0.4%.
[b] The yield based on selenium, [c] The structure confirmed by ^{1}H NMR in solution. In the solid state the compound forms linear polymer[22]. [d] Softening point. [e] Selenides (recrystallized from the same solvents as corresponding diselenides), m.ps. [°C] - 4f m.p.45, lit[25] oil b.p. 135-140/0.5 mm, 4j m.p. 174, 4k m.p. 127, 4l m.p. 87, 4p m.p. 137, 4q m.p. 132, 4r m.p. 112, 4s m.p. 193, 5 selenide of formula $(CH_3)_3SiSeSi(CH_3)_3$ b.p. 181/760, lit[21] b.p. 45-46/5.3 . [f] 2,3-Dihydrobenzoselenophene-3-one of formula  m.p. 75°C (hexane). [g] The yield based on trimethylsilyl chloride.

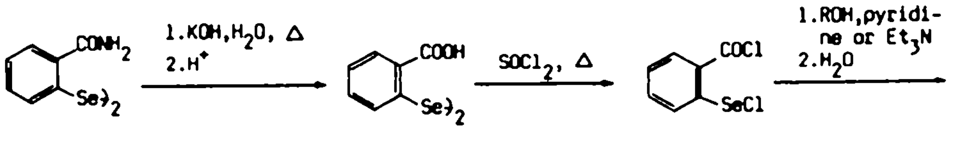
Table 2. IR and ^{1}H-NMR Data of New Diselenides 1-3 and Selenides 4, 6.

Compound	IR (KBr) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR (CDCl$_3$) δ (ppm) TMS
1a	-	[a] 3.90 (quintet, 2H, J=5Hz, $-CH_2-$); 4.35 (t, 4H, J=5Hz, $-CH_2Se-$).
1c	-	3.53 (q, 4H, J=10Hz, $-CH_2-$).
1d	-	1.17 (t, 12H, J=8Hz, $-CH_3$); 3.16 (d, 4H, J=6Hz, $-CH_2Se-$); 3.42-3.72 (m, 4H, $-CH_2O-$); 4.67 (t, 2H, J=6Hz, $-\overset{\vert}{C}H-$).
1j	2225[b]	7.44 (dd, 2H, J=2Hz and 8Hz, ArH); 7.64 (dt, 4H, J=2Hz and 8Hz, ArH); 7.88 (dd, 2H, J=2Hz and 8Hz, ArH).
1k	1649	7.30-7.40 (m, 4H, ArH); 7.22-7.84 (m, 4H, ArH); 10.12 (s, 2H, CHO).
1l	1654	2.68 (s, 6H, $-CH_3$); 7.22-7.37 (m, 4H, ArH); 7.82-7.99 (m, 4H, ArH).
1m	1685	c -
1o	1616 3300[d]	2.90 (d, 6H, J=5Hz, $-CH_3$); 7.30-7.52 (m, 4H, ArH) ; 7.68-7.96 (m, 4H, ArH); 8.66-8.90 (m, 2H, -NH-).
1p	1618	0.90 (t, 6H, J=7Hz, $-CH_3$); 1.26 (s, 36H, $-CH_2-$); 1.54-1.74 (m, 4H, $-CH_2-$); 3.50 (q, 4H, J=7Hz, $-\overset{\vert}{N}CH_2-$); 6.20 (t, 2H, J=7Hz, -NH-); 7.20-7.36 (m, 4H, ArH); 7.40-7.56 (m, 2H, ArH); 7.90-7.98 (m, 2H, ArH).
1q	1618 3395[d]	0.95 (t, 6H, J=7Hz, $-CH_3$); 1.24 (s, 64H, $-CH_2-$); 3.42 (m, 4H, ($-\overset{\vert}{N}CH_2-$); 6.26 (broad s, 2H, -NH-); 7.18-7.32 (m, 4H, ArH); 7.42-7.54 (m, 2H, ArH); 7.86-7.96 (m, 2H, ArH).
1r	1600	3.05 (broad s, 12H, $-CH_3$); 7.20-7.40 (m, 6H, ArH); 7.76-7.94 (m, 2H, ArH).
1s	-	7.46-7.80 (m, 8H, ArH); 7.92-8.08 (m, 4H, ArH).
1t	1715[e]	1.30 (t, 6H, J=7Hz, $-CH_3$); 3.74 (s, 4H, $-CH_2Se-$); 4.22 (q, 4H, J=7Hz, $-CH_2O-$).
1u	1715[e]	1.27 (t, 6H, J=7Hz, $-CH_3$); 2.82 (dt, 4H, J=1.5Hz and 6Hz, $-CH_2Se-$); 3.12 (dt, 4H, J=1.5Hz and 6Hz, $-COCH_2-$); 4.16 (q, 4H, J=7Hz, $-CH_2O-$).

Compound	IR (KBr) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm) TMS
1w	-	1.04 (t, 6H, J=7Hz, $-CH_3$); 2.58 (q, 4H, J=7Hz, $-\underline{CH_2}CH_3$); 2.72-3.17 (m, 8H, $-CH_2CH_2-$).
1x	-	5.07 (s, 1H, -CH-); 7.30 (s, 10H, ArH).
2	3340(broad)^{ef}	1.26 (d, J=6Hz, $-CH_3$); 3.03 (dd, 4H, $-SeCH_2-$); 3.67 (s, 2H, -OH); 3.86-4.10 (m, 2H, -CH-).
3	1680, 1700 2500 -3100^f	c —
4f	-	7.09 (q, 2H, J=4.5Hz, 5-H); 7.42-7.54 (m, 4H, 3-H and 4-H); 8.46 (dt, 2H, J=4.5Hz and 1Hz, 6-H).
4j	2235^b	7.45-7.80 (m, 8H, ArH).
4k	1652, 1681	7.20-7.50 (m, 6H, ArH); 7.90-8.00 (m, 2H, ArH); 10.22 (s, 2H, CHO).
4l	1652	2.56 (s, 6H, $-CH_3$); 7.22-7.36 (m, 6H, ArH); 7.58-7.82 (m, 2H, ArH).
4p	1620, 1628 3252^d, 3365^d	0.90 (t, 6H, J=7Hz, $-CH_3$); 1.26 (s, 36H, $-CH_2-$); 1.30-1.62 (m, 4H, $-CH_2-$); 3.32 (q, 4H, J=7Hz, $-NCH_2-$); 6.75 (t, 2H, J=7Hz, -NH-); 7.20-7.46 (m, 6H, ArH); 7.60-7.74 (m, 4H, ArH).
4q	1612, 1616	0.90 (t, 6H, J=7Hz, $-CH_3$); 1.26 (s, 64H, $-CH_2-$); 3.22 (q, 4H, J=7Hz, $-NCH_2-$); 6.64 (t, 2H, J=7Hz, -NH-); 7.26-7.48 (m, 6H, ArH); 7.63-7.74 (m, 4H, ArH).
4r	1612	2.86 (s, 6H, $-CH_3$); 3.08 (s, 6H, $-CH_3$); 7.22-7.34 (m, 6H, ArH); 7.42-7.54 (m, 2H, ArH).
4s	-	7.48-7.88 (m, 8H, ArH); 8.00-8.14 (m, 4H, ArH);
6	1675, 1687	3.82 (s, 2H, $-CH_2-$); 7.10-7.28 (m, 1H, ArH); 7.47 (dd, 2H, J=2Hz and 3Hz, ArH); 7.70 (dd, 1H, J=2Hz and 8Hz, ArH).

[a] Spectrum measured in $CHBr_3$; [b] $\nu_{C\equiv N}$; [c] Compound insoluble in the solvent used in NMR spectroscopy; [d] ν_{NH}; [e] Spectrum taken in film; [f] ν_{OH}

The additional problem concerned synthesis of bis(o-carboxyalkylphenyl) diselenides 8, particularly these having lipophilic aliphatic chain, expected to be phase transfer activators of hydrogen peroxide. All attempts to substitute the halogen atom in o-chloro- or o-iodobenzoate with the diselenide ion were unsuccessful. The reaction did not proceed at all or under more severe conditions bis(2-carboxyphenyl) diselenide 1m was obtained in low yield. The more efficient way to 1m involved hydrolysis of amide 1n to corresponding acid 1m. According to published procedure[26], acid 1m was easily converted into chloride 7 which with appropriate alcohols gave desired bis(2-carboxyalkylphenyl) diselenides 8 (listed in Table 3).



1n 1m 7 8

The catalytic efficiency of aryl diselenides as activators of hydrogen peroxide is under detailed investigation and will be published elsewhere.

Table 3. Bis(o-carboxyalkylphenyl) diselenides 8

Compound	Yield	m.p. °C	IR (KBr) $\nu_{C=O}$, cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm) TMS	Molecular formula (Molecular weight)
8a	61	132^b	1688	1.43 (t, 6H, J=7Hz, $-CH_3$); 4.45 (q, 4H, J=7Hz, $-CH_2-$); 7.14-7.24 (m, 4H, ArH); 7.78-7.89 (m, 2H, ArH); 8.04-8.17 (m, 2H, ArH).	$C_{18}H_{18}O_4Se_2$ (456.3)
8b	35	164^b	1678	1.64 (s, 18H, $-CH_3$); 7.12-7.40 (m, 4H, ArH); 7.76--7.86 (m, 2H, ArH); 7.96-8.08 (m, 2H, ArH).	$C_{22}H_{26}O_4Se_2$ (512.5)
8c	65	72^c	1690	0.86 (t, 6H, J=7Hz, $-CH_3$); 1.24 (s, 36H, $-CH_2-$); 1.70-1.79 (m, 4H, $-CH_2-$); 3.98 (t, 4H, ArH); 7.78--7.88 (m, 2H, ArH); 8.02-8.12 (m, 2H, ArH).	$C_{38}H_{58}O_4Se_2$ (736.9)
8d	78	83^c	1690	0.88 (t, 6H, J=7Hz, $-CH_3$); 1.26 (s, 60H, $-CH_2-$); 2.74-2.98 (m, 4H, $-CH_2-$); 4.40 (t, 4H, J=6Hz, $-OCH_2-$); 7.20-7.26 (m, 4H, ArH); 7.80-7.90 (m, 2H, ArH); 8.04-8.16 (m, 2H, ArH).	$C_{50}H_{82}O_4Se_2$ (904.2)

[a] Satisfactory microanalysis obtained: C ± 0.4%, H ± 0.3%, Se ± 0.4%

[b] Recrystallized from hexane/AcOEt, [c] Recrystallized from hexane

EXPERIMENTAL

Capillary m.ps and b.ps are uncorrected. ^{1}H-NMR spectra were recorded on a Tesla 100 MHz apparatus. IR spectra were measured on a Perkin-Elmer 621 spectrophotometer.

Preparation of lithium diselenide. To pure tetrahydrofuran (50 ml) freshly distilled from a mixture sodium-benzophenone or from $LiAlH_4$, the fine slices of lithium (0.75 g, 0.107 mole) and diphenylacetylene (0.5 g, 2.8 mmol) were added under nitrogen. The reaction mixture was vigorously stirred for 1 h (it was turned deep blue after 10-15 min) and placed on a water bath. Practical grade selenium (8.0 g, 0.100 mole) was added in one portion and stirring was continued for 24 h. In the case when pure selenium (99.5% of purity) was used as a reagent, the reaction mixture was additionally refluxed for 1 h. The reddish-brown solution of lithium diselenide thus obtained, free from residual lithium, was used in subsequent experiments.

1,2-Diselenolane (1a). To a stirred solution of lithium diselenide (prepared from double amounts of the reagents), the solution of 1,3-dibromopropane (22 g, 0.109 mole) in THF (20 ml) was added dropwise under nitrogen at room temperature (water bath) during 15 min. Stirring was continued for additional 30 min and then the mixture was poured into water (200 ml), ethanol was added to disappearance of the organic layer and the reaction mixture was stirred for 3 h. The solid was filtered off, washed with ethanol and dried on the air to yield yellow powder 19.5 g (98%) being a polymeric form of compound 1a. It softened between 60-70°C, and was insoluble in common organic solvents except these having the bromine or iodine atoms in the molecule, such as CH_2Br_2, $CHBr_3$, $BrCH_2CH_2Br$, CH_3I, CH_2I_2 but also in benzene in the presence of catalytic amounts of a substance able to generate free radicals, such as I_2 and under UV irradiation. Crude product was purified by means of chromatography. Thus, this compound (5 g) was dissolved in $CHBr_3$ (10 ml), mixed with silica gel (20 ml) and poured into the column packed with silica gel. Initially hexane, then a mixture hexane-methylene chloride (7:3) was used as an eluent. Compound 1a depolymerized on silica gel and existed in solution as a monomer. When the solvent was evaporated it turned again into polymer (4.0 g, 98%) softening at 50-60°C. After three weeks of storage at room temperature, its softening point increased to 65-70°C. 1,2-Diselenolane was also obtained from 1,3-propanediol ditosylate in the same manner as described above.

4,4-Dimethyl-1,2-diselenolane (1b). To a stirred solution of lithium diselenide (prepared from double amounts of the reagents), the solution of 1,3-dibromo-2,2-dimethylpropane (23 g, 0.100 mole) or 2,2-dimethyl-1,3-propanediol dimesylate (27 g, 0.104 mole) in THF (20 ml) was added dropwise under nitrogen at room temperature during 15 min. Stirring was continued for additional

30 min at room temperature and for 2 h under reflux. The reaction mixture was cooled and poured into water (100 ml). Ethyl ether (100 ml) was added and the layers separated after shaking. The organic layer was washed twice with satd. aqueous NaCl and dried over Na_2SO_4. After the solvent was removed, the residue was distilled in vacuo (15 torr) and the fraction boiling at 180°C was collected as pure 1b (Table 1).

Bis(2,2,2-trifluoroethyl) diselenide (1c). To a stirred solution of lithium diselenide, the solution of 2-iodo-1,1,1-trifluoroethane (21 g, 0.100 mol) or 2,2,2-trifluoroethyl mesylate (18 g, 0.101 mol) or 2,2,2-trifluoroethyl tosylate (25.4 g, 0.100 mol) in THF (20 ml) was added dropwise under nitrogen at room temperature during 15 min. The stirring was continued for additional 30 min at room temperature and 1 h under reflux. The reaction mixture was worked up as described for 1b. Product distilled at 161°C under normal pressure to give pure 1c (Table 1) .

Bis(2,2-diethoxyethyl) diselenide (1d) was obtained from 1-bromo-2,2-diethoxyethane (21.5 g, 0.110 mole) in the same manner as 1c.

Diphenyl diselenide (1e). To a stirred solution of lithium diselenide, iodobenzene (22.5 g, 0.11 mole) and HMPT (30 ml) were added under nitrogen and volatile components of the mixture were distilled off. The reaction mixture was heated on an oil bath at 115-120°C under nitrogen for 22 h, and at 140-150°C for 28 h. After cooling, the mixture was poured into water (100 ml) and shaken with methylene chloride. An organic layer was separated, washed with water and dried over Na_2SO_4. The solvent was evaporated off in vacuo and crude product was purified by means of flash chromatography on silica gel using initially hexane and then a mixture hexane-methylene chloride (8:2) as the eluent.

Bis(2-pyridyl) diselenide (1f). To a solution of lithium diselenide, 2-bromopyridine (17 g, 0.107 mole) and HMPT (30 ml) were added and the mixture was stirred at room temperature for 24 h under nitrogen. The volatile components were distilled off and the reaction mixture was heated on an oil bath at 115-120°C for 4 h, cooled and worked up as described for 1e. Diselenide 1f and selenide 4f were isolated by means of column chromatography on silica gel using light petrol-ethyl ether (1:1) as an eluent.

Bis(2-nitrophenyl) diselenide (1g). The solution of lithium diselenide was added dropwise under nitrogen at room temperature to a stirred solution of 2-nitrochlorobenzene (17.3 g, 0.110 mole) in THF (40 ml) and HMPT (20 ml). The reaction was continued for 20 h. then water (30 ml) was added and the mixture was stirred for additional 30 min. Product 1g was filtered off, washed with water and dried on air.

Bis(4-nitrophenyl) diselenide (1h) was obtained from 4-nitrochlorobenzene (17.3 g, 0.11 mole) in the same manner as 1g. The reaction time was 24 h.

Bis(2,4-dinitrophenyl) diselenide (1i). The solution of lithium diselenide was added dropwise under nitrogen to a stirred solution of 2,4-dinitrochlorobenzene (23 g, 0.115 mole) in THF (70 ml) on the ice/water bath during 30 min. The reaction was continued for additional 30 min and product 1i was filtered off and washed subsequently with THF, water and methanol and dried in air.

Bis(2-cyanophenyl) diselenide (1j). To a solution of lithium diselenide o-chlorobenzonitrile (15 g, 0.110 mole) and HMPT (30 ml) were added and the mixture was stirred under nitrogen at 115-120°C, while the wolatile compounds were distilled off. The reaction was continued at this temperature for 6 h, then the mixture was poured into water (100 ml) and the product was filtered off, washed with water and dried in air. Crude product was dissolved in the hot mixture tetrachloromethane-chloroform and after cooling selenide 4j crystallized and was filtered off. The filtrate was concentrated to a small volume, tetrachloromethane was added and pure diselenide 1f was filtered off and dried in air.

Bis(2-formylophenyl) diselenide (1k). To a solution of lithium diselenide, o-chlorobenzaldehyde (17 g, 0.120 mole) and HMPT (30 ml) were added and the mixture was stirred under nitrogen at room temperature for 18 h and at 115-120°C for additional 6 h, while the volatile components were distilled off. After cooling, the reaction mixture was poured into water (100 ml) and extracted with methylene chloride. The extract was washed with water and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was separated by means of column chromatography on silica gel using light petrol-methylene chloride (1:1) as an eluent. Diselenide 1k was eluted as the first and selenide 4k as the second product.

Bis(2-acetylphenyl) diselenide (1l). To a stirred solution of lithium diselenide, o-chloroacetophenone (18 g, 0.115 mole) and HMPT (30 ml) were added under nitrogen with stirring at room temperature an the reaction was continued for additional 7 h at 115-120°C. After this time, the reaction mixture was cooled, poured into water (100 ml) and extracted with methylene chloride. The extract was washed with water, dried over Na_2SO_4 and the solvent evaporated off. From the crude product, diselenide 1l, and selenides 4l and 6 were isolated by means of column chromatography on silica gel using light petrol-methylene chloride (8:2) as an eluent. The products were eluted in order: 6, 1l, 4l.

Bis(2-carboxyphenyl) diselenide (1m) from ethyl 2-iodobenzoate. To a stirred solution of lithium diselenide, ethyl 2-iodobenzoate (30 g, 0.107 mole) and HMPT (30 ml) were added under nitrogen and the reaction mixture was heated to 115-120°C. The volatile components were distilled off, then the reaction was continued for 24 h and the mixture was poured into water (100 ml) and extracted with methylene chloride. The extract was washed twice with 10% aqueous NaOH and with water. The aqueous solutions were collected, filtered through celite and acidified with diluted HCl. The solid formed was filtered off and recrystallized from AcOH-dioxane to give pure acid 1m (4.6 g). The organic layer was dried over Na_2SO_4, the solvent was evaporated in vacuo and the residue was heated with 10% solution of KOH in methanol (100 ml). Methanol was evaporated in vacuo and the residue was treated with water. The mixture was extracted with methylene chloride. An organic layer was removed, aqueous layer was acidified with hydrochloric acid and solid was filtered off and recrystallized from AcOH-dioxane to give additional portion of pure 1m (0.9 g). The total yield of pure 1m was 5.5 g (28%).

Bis(2-carboxyphenyl) diselenide (1m) from bis(2-carboxamidophenyl) diselenide (1n). The complex of 1n with DMF (12.6 g, 23 mmol) and the solution of KOH (25 g, 0.15 mole) in water (200 ml) were heated under reflux for 22 h. Then the reaction mixture was cooled, filtered and the filtrate was acidified with 10% aqueous HCl. Crude product was filtered off and recrystallized from AcOH--dioxane to give pure acid 1m in 98% yield.

Bis(2-carboxamidophenyl) diselenide (1n). To a stirred solution of lithium diselenide, 2-iodobenzamide (27 g, 0.109 mole) and HMPT (30 ml) were added under nitrogen with stirring. The mixture was heated to 115°C and the volatile components were distilled off. The reaction mixture was maintained at 115-120°C for 19 h and it solidified when the reaction finished. After cooling, water (100 ml) was added the crude product filtered off, washed with water, dried in air and recrystallized from dioxane-DMF. The product obtained (19.1 g, 70%) was molecular adduct 1n-DMF in molar ratio 1:2, m.p. 234°C with decomp. This adduct was recrystallized from dioxane or propionic acid to give pure 1n.

Bis[2-(N-methylcarboxamido)phenyl] diselenide (1o) was obtained from 2-iodo-N-methylbenzamide (14 g, 0.054 mole) and lithium diselenide (prepared from half amount of the reagents) in HMPT (15 ml). The reaction conditions (Table 1) and method of product isolation were similar as for 1n.

Bis[2-(N-dodecylcarboxamido)phenyl] diselenide (1p) was obtained from 2-iodo-N-dodecylbenzamide (22 g, 0.054 mole) and lithium diselenide (prepared from half amount of the reagents) in HMPT (15 ml). The reaction conditions (Table 1) were similar as for 1n. After the reaction was finished, the mixture was poured into water (100 ml), methylene chloride (200 ml) was added under vigorous stirring and a mixture was allowed to stand for 20 h. The solid was filtered off, washed with dichloromethane and recrystallized from ethyl acetate to give pure diselenide 1p. From the filtrate an organic layer was separated, washed with water and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was dissolved in ethyl ether (30 ml). To this solution, hexane (70 ml) was added and it was allowed to stand for 12 h. The solid was crude diselenide 4p which was recrystallized from ethyl acetate.

2-Iodo-N-dodecylbenzamide was obtained from 2-iodobenzoyl chloride (8 g, 30 mmol) which was added portionwise to the solution of dodecylamine (6 g, 32 mmole) in chloroform (80 ml) and dry triethylamine (40 ml) during 20 min, and the mixture was heated under reflux for 3 h. The reaction mixture was poured into solution of HCl, obtained from concd. HCl (100 ml) and water (50 ml), and shaken. The warm layers were separated, organic layer was cooled to about 5°C and filtered through celite. From the filtrate chloroform was evaporated off in vacuo and the crude product was recrystallized from hexane to give pure 2-iodo-N-dodecylbenzamide in 97% yield (12.2 g), m.p. 88°C.

Bis[2-(N-octadecylcarboxamido)phenyl] diselenide (1q) was obtained from 2-iodo-N-octadecylbenzamide (27 g, 0.054 mole) and lithium diselenide (prepared from half amount of the reagents) in HMPT (15 ml). The reaction conditions (Table 1) were similar as for 1n. After the reaction was finished, a mixture was poured into water (100 ml) and the solid filtered off, dried in air, dissolved in hot methylene chloride and cooled to 5°C. The product precipitated was filtered off, treated with hot ethanol (250 ml) and filtered again. The filtrate was cooled, solid was separated and chromatographed on the column packed with silica gel. Elution with methylene chloride yielded diselenide 1q and 4q. The methylene chloride solution was concentrated in vacuo to a volume of about 30 ml, hexane (150 ml) was added and the mixture was allowed to stand for 12 h. The product was filtered off and separated by means of chromatography (in the same manner as described above) yielding additional portions of 1q and 4q. The total yields of both products are given in Table 1.

2-Iodo-N-octadecylbenzamide was obtained from octadecylamine (10 g, 37 mmol) and 2-iodobenzoyl chloride in the similar way as described for 2-iodo-N-dodecylbenzamide. The reaction time was 5 h. The pure amide (m.p. 92°C) was obtained in 88% yield (15.0 g).

Bis[2-(N,N-dimethylcarboxamido)phenyl] diselenide (1r) was obtained from 2-iodo-N,N-dimethylbenzamide (15 g, 0.55 mole) and lithium diselenide (prepared from half amount of the reagents) in HMPT (15 ml). The reaction conditions (Table 1) were similar as for 1n. After the reaction was finished, the reaction mixture was diluted with water (100 ml) and shaken with methylene chloride. The extract was washed with water, dried over Na_2SO_4, methylene chloride was evaporated in vacuo and diselenide 1r and selenide 4r were separated by means of chromatography on silica gel using chloroform-acetone as an eluent.

Bis(2-quinolyl) diselenide (1s) was obtained from 2-chloroquinoline (9g, 0.055 mole) and lithium diselenide (prepared from half amount of the reagents) in HMPT (15 ml). The reaction conditions (Table 1) were similar as for 1f. After the reaction was finished, the reaction mixture was poured into water (100 ml) and solid filtered off and dried in air. The crude product was dissolved in chloroform, filtered through celite and chloroform was evaporated in vacuo. Diselenide 1s and selenide 4s were separated by means of column chromatography on silica gel. Initially chloroform and then chloroform-diisopropyl ether (95:5) were used as the eluents.

Bis(carboxyethylmethyl) diselenide (1t) was obtained from ethyl chloroacetate (13 g, 0.106 mole) and lithium diselenide in similar manner as 1a under the reaction conditions given in Table 1. The reaction mixture was worked up as described for 1b and diselenide 1t was distilled in vacuo (0.1 torr) at 120°C.

Bis(2-carboxyethylethyl) diselenide (1u) was obtained from ethyl 3-bromopropionate (20 g, 0.110 mole) and lithium diselenide in the similar manner as 1a (the reaction conditions are given in Table 1). The reaction mixture was worked up as described for 1b and diselenide 1u was distilled in vacuo (0.1 torr) at 142°C.

Bis[2-(N,N-diethylamino)ethyl] diselenide (1w). To a stirred solution of lithium diselenide, the solution of 2-chloro-N,N-diethylamine (15 g, 0.110 mole) in THF (20 ml) was added dropwise under nitrogen at room temperature during 15 min. The reaction was continued for additional 2 h, then the mixture was refluxed for 30 min and then worked up as described for 1b. Diselenide 1t was distilled in vacuo (0.13 torr) at 124°C.

Bis(diphenylmethyl) diselenide (1x) was obtained from diphenylchloromethane (11 g, 0.054 mole) and diphenyl diselenide (prepared from half amount of the reagents) in similar way as 1w (the reaction conditions are given in Table 1). The crude product was recrystallized from hexane.

Bis(2-hydroxypropyl) diselenide (2) was obtained from propylene oxide (7 g, 0.120 mole) and lithium diselenide in similar manner as 1a under conditions given in Table 1. The reaction mixture was worked up as described for 1b and the crude product was distilled in vacuo (0.2 torr, 133°C to afford pure diselenide 2.

Bis(3-carboxypropyl) diselenide (3). To a stirred solution of lithium diselenide, the solution of γ-butyrolactone (9.4 g, 0.110 mole) in THF (20 ml) was added under nitrogen at room temperature during 15 min. The reaction was continued for additional 1 h, then the mixture was refluxed for 30 min. It was cooled, poured into water (100 ml) and shaken with ethyl ether.
The layers were separated the ethereal solution was washed with 10% aqueous KOH, and the water solutions were combined, acidified with 10% aqueous HCl, and extracted with methylene chloride.
The extract was washed with water, dried over Na_2SO_4, solvent was evaporated in vacuo and the product was recrystallized from isopropyl ether-ethyl acetate to give pure diselenide 3.

Trimethylsilyl selenide (5). A solution of lithium diselenide was added dropwise to a stirred solution of trimethylsilyl chloride (11 g, 0.100 mole) in THF (20 ml) at temperature -80°C during 10 min and the reaction was continued at this temperature for additional 10 min. The solvent was evaporated in vacuo and the residue was treated with light petrol and decanted (three portion, 50 ml each). Light petrol was distilled off through the Vigreux column, then selenide 5 was distilled without column under normal pressure at 181°C to give pure product in 73% (based on trimethylsilyl chloride). When reaction was carried out at -10°C selenide 5 was obtained in 69% yield.

Trimethylsilyl selenide was also obtained from lithium selenide. Thus trimethylsilyl chloride (13 g, 0.120 mole) and trifluoroboride etherate (1 ml, 8 mmol) were added in one portion to a stirred solution of lithium selenide in THF (30 ml) and the reaction was carried out at room temperature for 4 h. Then the reaction mixture was worked up in the same manner as described above, the pure selenide 5 was obtained in 78% yield (based on selenium). Lithium selenide was prepared from practical grade selenium (4 g, 0.050 mole). Lithium (0.8 g, 0.114 mole) and diphenylacetylene (0.5 g, 2.8 mmole) in the same manner as lithium diselenide.

Bis[(2-carboxyethyl)phenyl] diselenide (8a). Dichloride 7[26] 3 g, (12 mmole) was added portionwise to a stirred solution of ethanol (3 ml, 51 mmole) in pyridine (15 ml) at temperature about 5°C during 10 min and the reaction was continued for additional 30 min. The reaction mixture was poured into water (30 ml), solid was filtered off and washed with 5% aqueous HCl and again with water. Diselenide 8a obtained was dried in vacuo and recrystallized from hexane-ethyl acetate.

Bis[(2-carboxy-t-butyl)phenyl] diselenide (8b). Dichloride 7 (3.6 g, 14 mmole) was added portionwise to a stirred solution of t-butanol (4 ml, 42 mmole) in pyridine (20 ml) at temperature about 5°C during 45 min and the reaction was continued for 30 min, then at room temperature for 1 h. The reaction mixture was poured into water (30 ml) and extracted with methylene chloride. The extract was washed with 5% aqueous HCl, then with water and dried over Na_2SO_4. The solvent was evaporated in vacuo and diselenide 8b was recrystallized from hexane-ethyl acetate.

Bis[(2-carboxydodecyl)phenyl] diselenide (8c) was obtained from solution of dodecanol (4.5 g, 24 mole) in pyridine (15 ml) and dichloride 7 (30 g, 0.012 mole) at room temperature. The reaction proceeded for 30 min, then the mixture was worked up in the same manner as described for 8b and crude product was purified by column chromatography on silica gel with hexane-ethyl ether (95:5) as an eluent and recrystallized from hexane.

Bis[(2-carboxyoctadecyl)phenyl] diselenide (8d) was obtained from solution of octadecanol (2.3 g, 0.008 mole) in dry triethylamine (20 ml) and dichloride 7 (2 g, 0.08 mole) in the similar way as 8b. The crude product was purified in the same manner as 8c.

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