Pergamon

Tetrahedron, Vol. 53, No. 36, pp. 12147-12158, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00548-6

Chemoselective Reduction of Organoselenocyanates to Diselenides and Selenolates

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Abstract : Selenocyanates produce selenolates or diselenides on reaction with metal hydrides (NaH, $LiHBEt_3$, $LiBH_4$, $NaBH_4$). The former transformation is performed with 2 molar equivalents of sodium hydride or lithium triethyl borohydride or 1.25 molar equivalent of metal borohydrides. The second one is performed with lower amount of reducing agent (1 molar equivalent of sodium hydride or lithium triethyl borohydride or 0.25 equivalent of metal borohydrides). Intermediate formation of a selenol or a selenolate which reacts on the unreacted selenocyanate is suspected in the later transformation. © 1997 Elsevier Science Ltd.

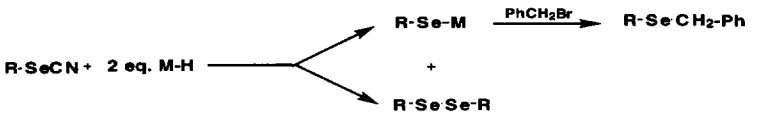
Organoselenocyanates play an important role in organoselenium chemistry. They are readily available, and stable compounds which are transformed to valuable basic organoselenium derivatives or reagents.[1] For example, aryl selenocyanates alone,[2] in the presence of an acid catalyst,[3] Cu(II) salts,[4] or tributyl phosphine[5,6] have been successfully used for the synthesis of selenides and functionalized selenides from organometallics[7] (Mg,[7a] Li,[7b] Hg[7c]), alkenes,[4a,b] alkynes,[4c,d] dienes,[4e,f] alcohols[6a,b] including allylic ones,[6c-e] aldehydes,[6f] enones and carboxylic acids.[6g] Organic selenocyanates are valuable precursors of (i) diselenides on reaction with alcoholates (ii) selenolates on reaction with sodium borohydride[8] or on alkaline hydrolysis,[1,9,13b] (iii) selenols on reaction with hypophosphorus acid,[10] (iv) selenenyl halides on reaction with halogens [9e,11a,c] or halogenating agents[11b] (v) selenosulfides on reaction with thiols[12] and (vi) seleninic acids on reaction with nitric acid,[13a] peracetic acid[13b] or potassium permanganate.[11b] Furthermore, α-silylalkyl selenocyanates react with tetrabutylammonium fluoride and lead to seleno aldehydes[14] and β-hydroxyalkyl selenocyanates, on reaction with bases, stereoselectively produce olefins.[15]

Few years ago, we found[16] that dialkyl diselenides are reduced to selenolates by sodium or potassium hydrides extending the reaction, first disclosed by Dowd,[17] on diphenyl diselenide (Scheme 1 a). This finding was particularly important for the synthesis and commercialization of selenomethionine.[18] We decided to generalize this reaction to organoselenocyanates hoping that these compounds will produce, even more smoothly, selenolates on reaction with sodium hydride (Scheme 1 b).

Scheme 1

We now report that organoselenocyanates react at 75°C, under argon, with a suspension of two molar equivalents of NaH in DMF to produce, almost instantaneously, the corresponding sodium selenolates. These have been further alkylated with benzyl bromide and lead to benzylselenides in reasonably good yields (Scheme 2, conditions A, entries a-d). The reaction has been successfully carried out on phenyl-, *prim*-alkyl and isopropyl- derivatives but does not occur with long chain sec-alkyl compounds such as 2-octyl- and 2-dodecyl selenocyanates which instead produce the corresponding diselenides (Scheme 2, entry e,f).

Scheme 2



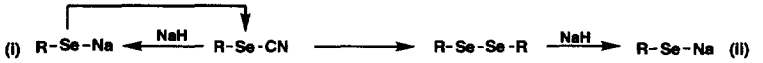
Entry	R	MH	Conditions A	Yield in $RSeCH_2Ph$	Yield in RSeSeR	Conditions B	Yield in $RSeCH_2Ph$	Yield in RSeSeR
a	Ph	NaH	DMF; 75°C; 0.5h	66		DMF; 20°C, 4h	66	
b	1-Bu	NaH	DMF, 75°C, 0.3h	75		DMF, 20°C, 3h	70	20
c	1-Dec	NaH	DMF; 75°C; 0.4h	75		DMF; 20°C, 3h	50	35
d	2-Pr	NaH	DMF; 75°C; 0.5h	63		DMF; 20°C, 21h		93
e	2-Dodec	NaH	DMF; 75°C; 1.5h		60	DMF; 20°C, 16h		90
f	2-Oct	NaH	DMF; 75°C; 1.5h		50			
g	1-Dec	KH				DMF; 20°C, 2h	80	
h	1-Bu	LiH	DMF; 75°C; 3 h		77	DMF; 20°C, 20h		66

Organoselenocyanates also react with 2 equivalents of sodium hydride at lower temperature. At 20°C, for example, the reaction is much slower and less chemoselective possessing a much higher propensity to generate diselenides (Scheme 2, conditions B). Thus, whereas phenyl selenocyanate, still produces efficiently the corresponding selenolate (Scheme 2, conditions B, entry a), *prim*-alkyl- and *sec*-alkyl-selenocyanates provide diselenides mixed with selenolates (Scheme 2, conditions B, entries b,c) or as the sole product (Scheme 2, conditions B, entries d,e; entry d, compare conditions B to A) respectively.

Related results have been obtained if sodium hydride is replaced by lithium or potassium hydrides or if the reactions are carried out in THF instead of DMF. Potassium hydride proved to be more reactive than sodium hydride in DMF and produces, already at 20°C, the corresponding selenolate in very good yield (Scheme 2, conditions B, compare entries g and c). In many cases however, not described here, the yields in selenolates were poorer with both hydrides than when sodium hydride was used. It is interesting to notice that lithium hydride constantly provided the diselenide (conditions A or B, Scheme 2, entry h).

As all these reactions have been carried out under an inert atmosphere, the formation of diselenides cannot be explained, by assuming the oxidation by air of an intermediate selenolate, as it has been previously often described.[19] Diselenides were therefore expected to result from the reaction of the first formed selenolates with the still unreacted selenocyanates (Scheme 3). Otherwise two discrete mechanisms might explain the formation of selenolates when two equivalents of hydride are used (Scheme 3). Organic selenolates can be formed directly on reaction of sodium hydride on the selenocyanate (Scheme 3, route (i)) or on reduction, by sodium hydride, of the diselenide intermediate (Scheme 3, route (ii)). In the later case, the selenolate formed must react faster on the starting selenocyanate than the hydride does. The formation of diselenides under conditions A (Scheme 2, entries e-f) and B (Scheme 2, entries b-e) could support, at least for these cases, the second mechanism.

Scheme 3



In order to test the validity of the mechanism involving organic diselenides as intermediates in the production of selenolates (see for example Scheme 2, conditions B, entry c), we have reacted didecyl diselenide with sodium hydride under conditions closely related to those used above on selenocyanates (2 eq. NaH, DMF, 20°C, 10 h) . We recovered the diselenide almost quantitatively.These results rule out, at least in this case, the intermediate formation of didecyl diselenide in the reaction of sodium hydride with decyl selenocyanate (Scheme 2, conditions B, entry c).

Since diselenides are expected to result from a competing reaction between the first formed selenolate with the still unreacted organoselenocyanate, one equivalent of sodium hydride should be left unreacted and therefore the formation of diselenides should require only one equivalent of sodium hydride.

We proved that this is indeed the case. Diselenides are best synthesized with 1 equivalent of sodium hydride in DMF at 20°C (Conditions C). The reaction is, as expected, faster (2-3h) with selenocyanates bearing an aryl group (Scheme 4; entry a) or a relatively small side chain (Scheme 4, Conditions C, entry b) and requires longer time (13-21 h) to go to completion with those derivatives bearing long- (Scheme 4, Conditions C, entry c) or branched side chains (Scheme 4, Conditions C, entries d-f).

Scheme 4

Entry	R	MH	Conditions C	Yield in RSeSeR	MH	Conditions D	Yield in RSeSeR
a	Ph	NaH	DMF, 20°C, 2h	77	LiH	THF, 75°C, 4h	80
b	1-Bu	NaH	DMF, 20°C, 3.5h	90	LiH	THF, 75°C, 4h	96
c	1-Dec	NaH	DMF, 20°C, 13h	70*			
d	2-Pr	NaH	DMF, 20°C, 3h	55	LiH	THF, 75°C, 20h	60
e	2-Dodec	NaH	DMF, 20°C, 16h	90			
f	2-Oct	NaH	DMF, 20°C, 12h	60			
g	1-Bu				NaH	THF, 75°C, 144h	93
h	1-Bu				KH	THF, 75°C, 108h	66

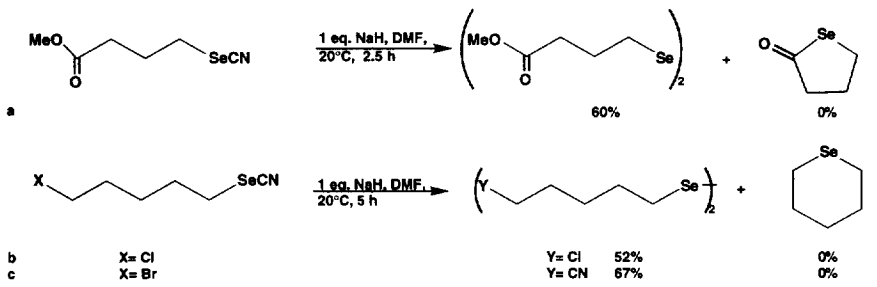
*This diselenide is produced in 30% yield after 2h.

The reaction of selenocyanates with one equivalent of alkali hydrides also provides, in THF, the corresponding diselenides (Scheme 4, conditions D). However, heating is required to achieve the reaction and lithium hydride proved now to be by far the most efficient reagent (Scheme 4, conditions D, entries b,g,h). The higher reactivity of lithium hydride accounts probably for its higher solubility in THF.

Sodium hydride (one equivalent) reacts successfully with functionalized selenocyanates such as methyl 4-selenocyanatobutanoate and 5-chloro- and 5-bromo-pentyl selenocyanates. It provides the related diselenides in good yield and free from the corresponding heterocycles (Scheme 5). Apparently, intermolecular reaction leading to the diselenide, which takes advantage of leaving group ability of the cyano group, is far better than the intramolecular one which would have instead produced one of the heterocycles shown on Scheme 5. The reaction is spectacular with 5-bromo-pentyl selenocyanate which still leads to the diselenide although one would have expected intramolecular substitution of the particularly good leaving group (Scheme 5, entry c). The formation of di-4(cyanopentyl) diselenide

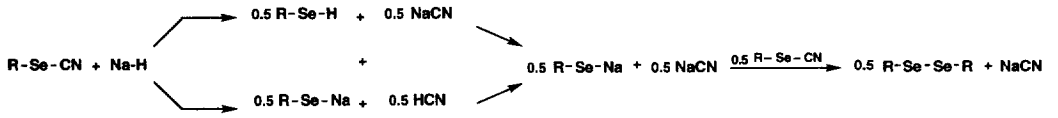
shows that the substitution of the bromine atom by the cyano group released in the medium is nevertheless smoothly achieved in the process (Scheme 5, entry c).

Scheme 5



These findings fully agree with the overall equation reported in Scheme 6 although the real mechanism still remains unclear.

Scheme 6



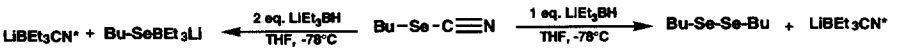
The results just disclosed lead us to read under a new light several papers which have been reported since 1975 on the reactivity of selenocyanates with borohydrides (sodium borohydride, lithium triethyl borohydride).[8,19,20] For example, very recently Salama described[19] that organoselenocyanates react with one molar equivalent of lithium triethyl borohydride or diisobutyl aluminum hydride to produce diselenides. He clearly mentioned that the diselenides result from the air oxidation of first formed selenols.[19] A careful copy of the scheme published by Salama[19] is reproduced in our Scheme 7.

Scheme 7

We suspected that the reaction between organoselenocyanates and lithium triethyl borohydride does not require the "air oxidation step" and that diselenides and not the selenols, as described by Salama,[19] are directly produced in a process related to the one we shown above with sodium hydride.

For that purpose, we have monitored by ^{77}Se NMR, and under argon, the reaction between butyl selenocyanate and *one molar equivalent* of lithium triethyl borohydride in THF, exactly as published by Salama. Di(*n*-butyl) diselenide was, as expected, exclusively detected. The reaction mixture contains neither butyl selenol nor the corresponding selenolate and therefore Salama's report is, as far as we know, erroneous. As a complementary result, we have indeed confirmed Salama's report[19] concerning the formation of complexed lithium butyl selenolate when *two molar equivalents* of lithium triethyl borohydride are instead used (Scheme 8).

Scheme 8



* We have no proof but NMR evidences that lithium cyanide and lithium butyl selenolates are complexed.

Finally, we turned our attention to the well known reduction of selenocyanates by metal borohydrides.[1b-e,8,20] We have checked carefully, in the absence of oxygen, the influence of the stoichiometry of the reagents on the outcome of the reaction. The results obtained with *n*-butyl selenocyanate and sodium borohydride in ethanol or lithium borohydride in THF are gathered in Scheme 9.

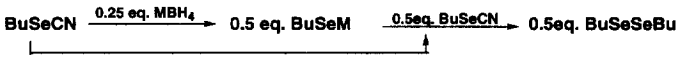
Scheme 9

Entry	MBH_4	Eq.	Conditions	BuSeSeBu	$BuSeBH_3M$ ($BuSeCH_2Ph$)*	BuSeCN (recovered)
a	$NaBH_4$	0.25	EtOH, 20°C, 0.3h	73	-	-
b	$NaBH_4$	0.5	EtOH, 20°C, 0.3h	17	45	-
c	$NaBH_4$	1.25	EtOH, 20°C, 0.3h		85	
d	$NaBH_4$	2	EtOH, 20°C, 0.3h	-	91	-
e	$LiBH_4$	0.25	THF, 20°C, 1h	74	-	21
f	$LiBH_4$	0.25	THF, 20°C, 48h	85	-	-
g	$LiBH_4$	0.5	THF, 20°C, 30h	21	40	-
h	$LiBH_4$	1.25	THF, 20°C, 23h	-	89	-
i	$LiBH_4$	2	THF, 20°C, 1h	-	88	-

*The resulting mixture is reacted with benzyl bromide for 2-5h.

A first significant result appears : use of 0.25 equivalent of the reducing agent (Scheme 9, entries a,e,f) affords exclusively the diselenide in good yields. Such results are easily rationalized by assuming that the four hydrides present on the reagents are efficiently transferred leading, whatever can be the real sequence of the events, to 0.5 equivalent of the selenolates which are then quenched with the unreacted selenocyanate (Scheme 10).

Scheme 10



Accordingly, 0.5 equivalent of borohydrides could have been just enough to produce quantitatively the butyl selenolate if (i) the second step described in Scheme 10 would have been substantially slower than the first one or if (ii) the starting *n*-butyl selenocyanate or the di(*n*-butyl) diselenide produced at the end of the whole process would have had a similar behavior towards borohydrides. This proved not to be the case since under these conditions a mixture of selenolate and the corresponding diselenide is obtained (Scheme 9, entries b,g) and therefore both of the above assumptions are, at least in this specific example, inoperative. Clearly, the reaction between the selenolate and the selenocyanate is a fantastically fast competing process.

In fact, we shown, in a control experiment, that the quantitative reduction of di(*n*-butyl) diselenide requires at least two equivalents of sodium borohydride in ethanol (Scheme 11).

Scheme 11

Entry	n eq.	$BuSeCH_2Ph$	BuSeSeBu (recovered)
a	0.5	20	44
b	1	35	30
c	1.5	60	15
d	2	87	0

All these findings fully support the results described in Scheme 9 (entries c,h), indicating that the complete transformation of *n*-butyl selenocyanate into the corresponding selenolate requires the use of at least 1.25 eq. of borohydride as described in the formal equation proposed in Scheme 12.

Scheme 12

$$BuSeCN \xrightarrow{0.25\ eq.\ MBH_4} 0.5\ eq.\ BuSeSeBu \xrightarrow{1\ eq.\ MBH_4} 1eq.\ BuSeM$$

Although we have clearly outlined, on some specific examples, the exact amount of borohydride needed to produce either the diselenide or the selenolate, we must admit at that stage that the reduction of organoselenocyanates by borohydrides is a rather complicated process. The figures depicted above may not be general and therefore further studies are obviously required.

For example, we have tried to perform some of the individual reactions which would have taken place in the reduction of butyl selenocyanate with metal borohydrides in THF. Obviously a series of cyanoborohydrides ($MBH_{4-n}(CN)_n$, $1 \leq n < 4$) complexed or not by the selenolate are intermediate in the transformation. Some have been widely used in organic synthesis (sodium cyanoborohydride)[21] whereas others are known but possess a very low reactivity (sodium dicyanoborohydride).[22]

In order to test these hypotheses, we have reacted sodium cyanoborohydride in ethanol with butyl selenocyanate under the conditions used with sodium borohydride (20°C, 3h). Di(*n*-butyl) diselenide was formed as expected, but the yield was dramatically low (10%). Decent results were only obtained if an excess of reagent was used, for much longer time, than those used in the model reaction. Apparently, the reaction is feasible but the conditions are fare more drastic than the ones which should have been required if this individual step was part of the reaction involving sodium borohydride (Scheme 9, entry a). We must therefore admit that another transient species is involved, maybe in competition with $NaBH_3CN$, in these reactions and that further work is needed to understand properly the process.

In conclusion we have described that selenocyanates are valuable precursors of selenolates or diselenides on reaction with metal hydrides (NaH, $LiHBEt_3$, $LiBH_4$, $NaBH_4$). The nature of the product formed highly depends upon the amount of hydride used. Two molar equivalents of sodium hydride or lithium triethyl borohydride or 1.25 molar equivalent of metal borohydride are strictly required for the production of the selenolates whereas the reaction stops at the diselenide stage when lower amount of reducing agent (1 molar equivalent of sodium hydride or lithium triethyl borohydride or 0.25 equivalent of metal borohydride) is instead used. We have some evidence that selenols or selenolates are intermediates in the later process and that they have a surprisingly very high propensity to react on the non reacted selenocyanates.

The organoselenolates used in this work have been prepared according to published procedures from the phenyl diazo derivative or alkyl- and functionalized alkyl halides and potassium selenocyanate in DMF (Schemes 13,14).[1,19,23-25] The reaction is quite slow at 20°C, works with most alkyl bromides and iodides but not with alkyl chlorides or with long chain *sec*-alkyl bromides (Scheme 13). It is much more efficient and faster when carried out at 75-90°C but use of a higher temperature is deleterious. Reaction of 1-5-dibromo-pentane and potassium selenocyanate led to 5-bromo-1-pentyl selenocyanate (46 %)[23] besides 1,5-diselenocyanato-pentane (25%) and some starting 1,5-dibromo-pentane (25 %, Scheme 14).

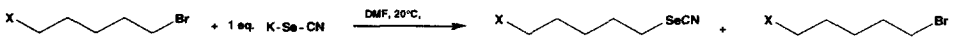
Scheme 13

$$R\text{-}X + K\text{-}Se\text{-}CN \xrightarrow{DMF} R\text{-}Se\text{-}CN$$

Entry	R-X	Yields
a	1-Bu-Cl	0 % (20°C, 20h), 90 % (75°C, 4h)[23]
b	1-Bu-Br	93 % (20°C, 24h)[23]
c	1-Dec-Br	90 % (20°C, 20h), 90 % (75°C, 3h)[23]

Entry	R-X	Yields
d	2-Pr-I	79 % (20°C, 20h)[24]
e	2-Dodec-Br	0 % (20°C,15 h), 90 % (90°C, 2h)
f	2-Oct-Br	84 % (90°C, 13h)
g	Br-$(CH_2)_3$-C(=O)-OMe	45 % (75°C, 3h)[19]

Scheme 14[19]



Entry	X	Conditions	X	Yield	Starting Material (recovered)
a	Cl	20°C, 21h	Cl	87%	-
b	Br	20°C, 48h	Br SeCN	46% 25%	25%

EXPERIMENTAL SECTION

General

^{1}H-NMR and ^{77}Se-NMR spectra have been performed on JEOL JNM EX 400 (400 MHz for ^{1}H or 76.24 MHz for ^{77}Se) or JEOL JNM EX-90 (16.93 MHz for ^{77}Se) spectrometers. The spectra were measured in $CDCl_3$ with TMS as an internal standard (^{1}H-NMR) and with MeSeMe as external reference (^{77}Se-NMR), δ are given in ppm. IR data (cm^{-1}) were obtained on neat liquids using a Perkin-Elmer model 337 or a BIO-RAD model FTS 165 spectrophotometer. Mass spectra were obtained on an HP 5995A GC-MS spectrometer. In the discussion, M refers to $M^{+\bullet}$ and only a few characteristics are reported. Microanalyses were performed in the Microanalysis Laboratory of the Paris VI University (Paris, France). Reactions performed at -78°C have been carried out in a flask immersed in a Dewar filled with acetone-dry ice mixture.

Reagents and solvents

The reagents and some solvents such as THF have been purchased from Acros (Geel, Belgium) except lithium borohydride and lithium triethyl borohydride which have been purchased from Aldrich (Antwerpen, Belgium). Ether and pentane were obtained from Roland (Bruxelles, Belgium). Anhydrous THF was distilled from sodium-benzophenone ketyl just prior use. Phenyl-[8] and alkyl selenocyanates,[19,22-25] used in this work, were prepared by known procedure from potassium selenocyanate and phenyl diazonium salt or alkyl halides. Diphenyl diselenide has been compared to a commercially available sample (Acros, Aldrich).

General Procedures

A. Synthesis of Alkyl selenocyanates.

Potassium selenocyanate (8.64 g, 60 mmol) and DMF (30 ml) are placed into a 250 ml two-necked flask fitted with a magnetic stirrer, a septum and a condenser connected to an argon filled balloon. The suitable alkyl halide is slowly introduced by a syringe (60 mmol in 10 ml DMF). The solution is stirred at 20°C for 24 h or heated under stirring to 75 °C for 3 h, then hydrolyzed (30 ml water) and extracted twice with 50 ml portions of ether. The ethereal fractions are combined, washed with water (3 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is fractionated by column chromatography on silica gel using pentane as eluent until the dialkyl diselenide comes out, then a pentane/ether: 8/2 mixture is used.

B. Cleavage of selenocyanates by one equivalent of MH (M= Na, K, Li)

MH (2 mmol) and DMF (1 ml) are introduced in a two-necked flask fitted with a magnetic stirrer and a septum connected to an argon filled balloon. The suitable alkyl selenocyanate is slowly introduced by a syringe (2 mmol in 1 ml DMF). The resulting mixture is stirred for 2-21h at 20 °C, then hydrolyzed (water, 10 ml) and extracted twice with 20 ml portions of ether. The ethereal fractions are combined, washed with water (2 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is fractionated by column chromatography on silica gel using pentane as eluent.

C. Cleavage of selenocyanates by two equivalents of MH (M= Na, K, Li)

MH (4 mmol) and DMF (1 ml) are introduced in a two-necked flask fitted with a magnetic stirrer, a septum and a condenser connected to an argon filled balloon. The suitable alkyl selenocyanate is slowly introduced by a syringe (2 mmol in 1 ml DMF). The mixture is stirred for 2-21h at 20 °C or for 0.3-3 h at 75 °C, then benzyl bromide (2 mmol in 1 ml DMF) is added. The resulting mixture is stirred for 2 h at 20 °C, then hydrolyzed (water, 10 ml) and extracted twice with 20 ml portions of ether. The ethereal fractions are combined, washed with water (2 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is fractionated by column chromatography on silica gel using pentane as eluent.

D. Cleavage of selenocyanates by one equivalent of lithium triethyl borohydride.

Selenocyanates (1 mmol) and THF (15 ml) are introduced in a two-necked flask fitted with a magnetic stirrer ,a septum and connected to an argon filled balloon. The flask is cooled at -78 °C and $LiBEt_3H$ (1,0 M, 1 ml) is slowly introduced by a syringe. The mixture is stirred for 0.25 h at -78 °C, then the cooling bath is removed and room temperature is slowly reached. The resulting mixture is stirred at 20 °C for 2 h, then hydrolyzed (water, 10 ml) and extracted twice with 20 ml portions of ether. The ethereal fractions are combined, washed with water (2 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is filtered on a pad of silica using pentane as eluent. The solvent is evaporated *in vacuo*.

E. Cleavage of *n*-butyl selenocyanate by one and two equivalents of lithium triethyl borohydride for NMR study.

n-Butyl selenocyanate (2 mmol) and THF (2 ml) are introduced into a 10 mm NMR tube. A slow stream of argon is passed for a few minutes then the tube is closed by a septum and cooled at -78 °C. $LiBEt_3H$ (1 M in THF, 1 ml) is slowly introduced by a syringe. The mixture is stirred at -78 °C for 0.25 h and the ^{77}Se NMR spectrum is recorded at that temperature. Another equivalent of $LiBEt_3H$ (1 M in THF, 1 ml) is then slowly introduced by a syringe. The mixture is stirred at -78 °C for 0.25 h then the ^{77}Se NMR spectrum is taken at that temperature. *n*-Butyl diselenide (+292 ppm) and *n*-butyl selenolate (-226 ppm) are respectively observed after addition of one or two equivalents of lithium triethyl borohydride.

F. Cleavage of *n*-butyl selenocyanate by 0.5-2 equivalents of sodium borohydride.

n-Butyl selenocyanate (2 mmol) and ethanol (2 ml) are introduced in a two-necked flask fitted with a magnetic stirrer, a septum and connected to an argon filled balloon. $NaBH_4$ (1-4 mmol) is added in small portions. The mixture is stirred at 20 °C for 0.25 h then benzyl bromide (342 mg, 2 mmol in ethanol, 1 ml) is added. The resulting mixture is stirred at 20 °C for 2 h then hydrolyzed (water, 10 ml) and extracted twice with 20 ml portions of ether. The ethereal fractions are combined, washed with water (2 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is fractionated by column chromatography on silica gel using pentane as eluent to recover the dibutyl diselenide and the corresponding benzyl butyl selenide.

G. Cleavage of *n*-butyl selenocyanate by 0.5-2 equivalents of lithium borohydride.

n-Butyl selenocyanate (2 mmol) and THF (2 ml) are introduced in a two-necked flask fitted with a magnetic stirrer and a septum connected to an argon filled balloon. $LiBH_4$ (2 M, 0.5-2 ml) is slowly introduced by a syringe. The reaction is stirred for 1 h at 20 °C then the benzyl bromide (2 mmol in 1 ml THF) is added. The resulting mixture is stirred for 2 h at 20 °C then hydrolyzed (water, 10 ml) and extracted twice with 20 ml portions of ether. The ethereal fractions are combined, washed with water (2 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is fractionated by column chromatography on silica gel using pentane as eluent to recover the dibutyl diselenide and the corresponding benzyl *n*-butyl selenide.

Typical procedures.

Cleavage of selenocyanate by 0.25 equivalent of sodium borohydride.

n-Butyl selenocyanate (4 mmol) and ethanol (4 ml) are introduced in a two-necked flask fitted with a magnetic stirrer and a septum connected to an argon filled balloon. $NaBH_4$ (38 mg, 1 mmol) is added in small portions. The mixture is stirred at 20 °C for 0.25 h then the benzyl bromide (684 mg, 4 mmol in 1 ml ethanol) is added. The resulting mixture is stirred at 20 °C for 2 h then hydrolyzed (water, 10 ml) and extracted twice with 20 ml portions of ether. The ethereal fractions are combined, washed with water (2 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is fractionated by column chromatography on silica gel using pentane as eluent to afford the corresponding pure dibutyl diselenide as an oil.

Cleavage of selenocyanate by 0.25 equivalent of lithium borohydride.

n-Butyl selenocyanate (2 mmol) and THF (2 ml) are introduced in a two-necked flask fitted with a magnetic stirrer and a septum connected to an argon filled balloon. $LiBH_4$ (2 M, 0.25 ml) is slowly introduced by a syringe. The reaction is stirred for 1 h at 20 °C then the benzyl bromide (2 mmol in 1 ml THF) is added. The resulting mixture is stirred at 20 °C for 2 h then hydrolyzed (water, 10 ml) and extracted twice with 20 ml portions of ether. The ethereal fractions are combined, washed with water (2 x 20 ml) and dried over $MgSO_4$. The solvent is evaporated *in vacuo*. The crude mixture is

fractionated by column chromatography on silica gel using pentane as eluent to afford the corresponding pure dibutyl diselenide.

n-Butyl selenocyanate [23] (93 %, as an oil) is prepared according to the general procedure A. *n*-Butyl bromide is introduced by a syringe (8.21 g, 60 mmol in 10 ml DMF) to the solution of potassium selenocyanate. The mixture is stirred at 20 °C for 17 h. R_f 0.8 (ether/pentane: 2/8). IR (neat) 2959, 2932, 2872, 2151, 1464, 1437, 1419, 1380, 1259, 1207, 1098, 1049, 737 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0,97 (t, 3H, J = 7.5 Hz, CH_3-CH_2), 1.4-1.53 (m, 2H, CH_3-CH_2), 1.85-1.95 (m, 2H, CH_3-CH_2-CH_2), 3.06 (t, 2H, J = 7.5 Hz, CH_2-SeCN). ^{77}Se-NMR ($CDCl_3$) δ = 208. Mass spectrum 163 (M), 106 (M - CH_3-$(CH_2)_3$), 57 (CH_3-$(CH_2)_3$). Analysis for C_5H_9NSe : calculated (C 37.05; H 5.60; N 8.64 %), found (C 37.07; H 5.58; N 8.75%).

n-Decyl selenocyanate[23] (83 %, as an oil) is prepared according to the general procedure A. *n*-Decyl bromide is introduced by a syringe (13.26 g, 60 mmol in 10 ml DMF) to the solution of potassium selenocyanate. The mixture is stirred at 20 °C for 26 h. R_f 0.75 (ether/pentane: 2/8). IR (neat) 2925, 2853, 2151, 1465, 1419, 1377, 1241 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0.9 (t, 3H, J = 6.3 Hz, CH_3-CH_2), 1.1-1.7 (m, 14H, CH_3-$(CH_2)_7$), 1.7-2.1 (m, 2H, CH_2-CH_2-SeCN) 3.1 (t, 2H, J = 7.5 Hz, CH_2-SeCN). ^{77}Se-NMR ($CDCl_3$) δ = 219. Mass spectrum 220 (M-HCN), 85 (CH_3-$(CH_2)_5$), 57 (CH_3-$(CH_2)_3$). Analysis for $C_{11}H_{21}NSe$: calculated (C 53.65; H 8.60; N 5.69 %), found (C 53.62; H 8.74; N 5.63 %).

Isopropyl selenocyanate [24] (75 %, as an oil) is prepared according to the general procedure A. Isopropyl bromide is introduced by a syringe (13.26 g, 60 mmol in 10 ml DMF) to the solution of potassium selenocyanate. The mixture is stirred at 20 °C for 20 h. R_f 0.77 (ether/pentane: 2/8). IR (neat) 2967, 2927, 2869, 2150, 1674, 1457, 1388, 1373, 1221, 1156, 1041, 932, 877 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 1.65 (d, 6H, J = 6.8 Hz, 2 CH_3), 3.7-3.8 (m, 1H, CH). ^{77}Se-NMR ($CDCl_3$) δ = 334. Mass spectrum 149 (M), 122 (M-HCN), 106 (M - $(CH_3)_2$-CH), 80. Analysis for C_4H_7NSe : calculated (C 32.45; H 4.77; N 9.46 %), found (C 32.54; H 4.62; N 9.28 %)

2-Dodecyl selenocyanate (83%, as an oil) is prepared according to the general procedure A. 2-Dodecyl bromide is introduced by a syringe (2.49 g, 10 mmol in 2 ml DMF) to the solution of potassium selenocyanate (1.71 g, 10 mmol in 5 ml DMF). The mixture is stirred at 20 °C for 15 h and then heated at 90°C for 2 h. R_f 0.95 (ether/pentane: 2/8). IR (neat) 2928, 2853, 2151, 1459, 1380, 1121, 723 cm^{-1}.^{1}H-NMR ($CDCl_3$) δ = 0.88 (t, 3H, J = 6.6 Hz, CH_3-CH_2), 1.2-1.4 (m, 16H, CH_3-$(CH_2)_8$), 1.68 (d, 3H, J = 6.8 Hz, CH_3-CH), 1.75-1.9 (m, 2H, CH_2-CH(CH_3)SeCN), 3.4-3.6 (m, 1H, CH-SeCN). ^{77}Se-NMR ($CDCl_3$) δ = 307. Mass spectrum 248 (M-HCN), 169 (M-SeCN), 127 (CH_3-$(CH_2)_8$), 113 (CH_3-$(CH_2)_7$), 99 (CH_3-$(CH_2)_6$), 85 (CH_3-$(CH_2)_5$), 71 (CH_3-$(CH_2)_4$), 57 (CH_3-$(CH_2)_3$). Analysis for $C_{13}H_{25}NSe$: calculated (C 56.92; H 9.19; N 5.11 %), found (C 57.03; H 9.16; N 4.98 %)

2-Octyl selenocyanate (84%, as an oil) is prepared according to the general procedure A. 2-Octyl bromide is introduced by a syringe (7.72 g, 40 mmol in 10 ml DMF) to the solution of potassium selenocyanate (5.76 g, 40 mmol in 30 ml DMF). The mixture is stirred at 90°C for 13 h. R_f 0.95 (ether/pentane: 2/8). IR (neat) 2958, 2929, 2858, 2149, 1719, 1459, 1380, 1260, 1235, 1143, 725 cm^{-1}.^{1}H-NMR ($CDCl_3$) δ = 0.9 (t, 3H, J = 6.6 Hz, CH_3-CH_2), 1.2-1.5 (m, 8H, CH_3-$(CH_2)_4$), 1.68 (d, 3H, J = 6.8 Hz, CH_3-CH), 1.7-1.9 (m, 2H, CH_2-CH), 3.5-3.6 (m, 1H, CH-SeCN). ^{77}Se-NMR ($CDCl_3$) δ = 313. Mass spectrum 219 (M), 192 (M-HCN), 113 (M-SeCN), 71 (CH_3-$(CH_2)_4$), 57 (CH_3-$(CH_2)_3$). Analysis for $C_9H_{17}NSe$: calculated (C 49.54; H 7.85; N 6.42 %), found (C 49.72; H 7.81; N 6.51 %)

Methyl 4-selenocyanatobutanoate[19] (45 %, as an oil) is prepared according to the general procedure A. Methyl 4-chlorobutanoate is introduced by a syringe (8.20 g, 60 mmol in 10 ml DMF) to the solution of potassium selenocyanate. The mixture is stirred at 75 °C for 3 h. R_f 0.18 (ether/pentane: 2/8). IR (neat) 3446, 2996, 2951, 2848, 2151, 1734, 1436, 1368, 1313, 1213, 1375, 1134, 1055, 1026, 991, 874, 856, 774, 746 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 2.2-2.3 (m, 2H, CH_2-CH_2-CH_2), 2.53 (t, 2H, J = 6.7 Hz, CH_2-C=O), 3.1 (t, 2H, J = 7.3 Hz, CH_2-Se), 3.7 (s, 3H, CH_3-O). ^{77}Se-NMR ($CDCl_3$) δ = 208. Mass spectrum 180 (M-HCN), 148 (M-CO_2-CH_3), 121 (M -HCN - CO_2-CH_3), 59 (CO_2-CH_3). Analysis for $C_6H_9NO_2Se$: calculated (C 34.97; H 4.40; N 6.80 %), found (C 35.10; H 4.36; N 6.65 %).

5-Chloropentyl selenocyanate (87 %, as an oil) is prepared according to the general procedure A. 1-Bromo-5-chloropentane is introduced by a syringe (5.23 g, 28 mmol in 10 ml DMF) to the solution of potassium selenocyanate (4.03 g, 28 mmol in 15 ml DMF). The mixture is stirred at 20 °C for 21 h. R_f 0.32 (ether/pentane: 2/8). IR (neat) 2938, 2862, 2150, 1457, 1452, 1417, 1307, 1283, 1264, 1235, 1209, 723, 649 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 1.6-1.7 (m, 2H, $(CH_2)_2$-CH_2-$(CH_2)_2$), 1.8-1.9 (m, 2H, CH_2-CH_2-SeCN), 1.9-2.0 (m, 2H, CH_2-CH_2-Cl), 3.07 (t, 2H, J = 7.3 Hz, CH_2-SeCN), 3.57 (t, 2H, J = 6.4 Hz, CH_2-Cl). ^{77}Se-NMR ($CDCl_3$) δ = 212. Mass spectrum 211 (M), 149 (M-HCl, -CN),107. Analysis for $C_6H_{10}ClNSe$: calculated (C 34.23; H 4.79; N 6.65 %), found (C 34.30; H 4.74; N 6.57 %).

5-Bromopentyl selenocyanate[19] (46 %, as an oil) is prepared according to the general procedure A.1,5-Dibromopentane is introduced by a syringe (13.80 g, 60 mmol in 10 ml DMF) to the solution of potassium selenocyanate. The mixture is stirred at 20 °C for 48 h. R_f 0.2 (ether/pentane: 2/8). We have also isolated pentyl diselenocyanate (25 %, as an oil) and dibromopentane (25 %, as an oil)). IR (neat) 2935, 2858, 2150, 1457, 1437, 1294, 1255, 1220 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 1.60-1.64 (m, 2H, $(CH_2)_2$-CH_2-$(CH_2)_2$), 1.90-1.97 (m, 4H, CH_2-CH_2-CH_2-CH_2-Cl), 3.07 (t, 2H, J = 7.3 Hz, CH_2-SeCN), 3.44 (t, 2H, J = 6.6 Hz, CH_2-Br). ^{77}Se-NMR ($CDCl_3$) δ = 212. Mass spectrum 256 (M), 255 (M-1), 228 (M-CN), 149 (M-SeCN), 69 (M-SeCN -Br). Analysis for $C_6H_{10}BrNSe$: calculated (C 28.26; H 3.96; N 5.49 %), found (C 28.38; H 3.90; N 5.56 %).

Di *n*-butyl diselenide (83 %, as an oil) is prepared according to the general procedure B. The *n*-butyl selenocyanate (324 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (60 mg, 80 % in 1 ml DMF). The resulting mixture is stirred for 3.5 h at 20°C, then treated. R_f 0,73 (pentane). IR (neat) 2955, 2925, 2869, 1462, 1410, 1376, 1291, 1253, 1188 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0.93 (t, 6H, J = 7.0 Hz, 2 x CH_3), 1.35-1.5 (m, 4H, 2 x (CH_3-CH_2), 1.7-1.8 (m, 4H, (-CH_2-CH_2-Se)$_2$), 2.92 (t, 4H, J = 7.5 Hz, (-CH_2-Se)$_2$). ^{77}Se-NMR ($CDCl_3$) δ = 313. Mass spectrum 274 (M), 160 (2 x CH_3-CH_2-)$_3$), 57 (CH_3-$(CH_2)_3$). Analysis for $C_8H_{18}Se_2$: calculated (C 35.31; H 6.67 %), found (C 35.34; H 6.69 %).

Di *n*-decyl diselenide (69 %, as an oil) is prepared according to the general procedure B. Decyl selenocyanate (492 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (60 mg, 80 % in 1 ml DMF). The resulting mixture is stirred at 20°C for 13 h, then treated. R_f 0.92 (pentane). IR (neat) 2953, 2931, 1464, 1410, 1376, 1292, 1265, 1234, 1217, 1196, 1176, 1115, 720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0.95 (t, 6H, J = 7.0 Hz, 2 x CH_3),1.1-1.95 (m, 32H, (-$(CH_2)_8$-CH_2-Se)$_2$), 2.87 (t, 4H, J = 7.3 Hz, (-CH_2-Se)$_2$). ^{77}Se-NMR ($CDCl_3$) δ = 308. Mass spectrum 442 (M), 99 (CH_3-$(CH_2)_6$), 85 (CH_3-$(CH_2)_5$), 71 (CH_3-$(CH_2)_4$), 57 (CH_3-$(CH_2)_3$). Analysis for $C_{20}H_{42}Se_2$: calculated (C 54.54; H 9.61 %), found (C 54.65; H 9.59 %).

Diisopropyl diselenide (55 %, as an oil) is prepared according to the general procedure B. Isopropyl selenocyanate (324 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (60 mg, 80 % in 1 ml DMF). The resulting mixture is stirred at 20°C for 3 h, then treated. Rf 0.65 (pentane). IR (neat) 2952, 2857, 1461, 1437, 1378, 1363, 1310, 1209, 1151, 1023, 925, 873 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 1.44 (d, 12H, J = 7.0 Hz, 2 x ($(CH_3)_2$-CH), 3.2-3.3 (m, 2H, (CH-Se)2). ^{77}Se-NMR ($CDCl_3$) δ = 402. Mass spectrum 246 (M), 204 (H-Se-Se-CH$(CH_3)_2$), 160 (SeSe), 107 (Se-CH=CH_2), 80. Analysis for $C_6H_{14}Se_2$: calculated (C 29.53; H 5.78 %), found (C 29.57; H 5.96 %).

Di-2-dodecyl diselenide (90 %, as an oil) is prepared according to the general procedure B. 2-Dodecyl selenocyanate (548 mg, 2 mmol in 0.5 ml DMF) is added to the suspension of NaH (130 mg, 80 % in 0.5 ml DMF). The resulting mixture is stirred at 20°C for 16 h, then treated. R_f 0.9 (pentane). IR (neat) 2553, 2920, 2852, 1457, 1373, 1137, 721 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0.85 (t, 6H, J = 6.6 Hz, 2 x (CH_3-CH_2-)), 1.2-1.35 (m, 28H, 2X (CH_3-$(CH_2)_7$)), 1.35-1.8 (m, 14H, (-CH_2-CH_2-CH(CH_3)-Se)$_2$), 3.0-3.1 (m, 2H, (-CH-Se)$_2$). ^{77}Se-NMR ($CDCl_3$) δ = 373.4 and 373.7. Mass spectrum 498 (M), 330 (CH_3-$(CH_2)_9$--CH(CH_3)-SeSeH), 58 (CH_3-$(CH_2)_3$ + 1). Analysis for $C_{24}H_{50}Se_2$: calculated (C 58.05; H 10.15 %), found (C 58.11; H 10.15 %)

Di-2-octyl diselenide (60 %, as an oil) is prepared according to the general procedure B. 2-Octyl selenocyanate (436 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (60 mg, 80 % in 1 ml DMF). The resulting mixture is stirred at 20°C for 3.5 h, then treated. R_f 0.57 (pentane). IR (neat) 2956, 2927, 2857, 1458, 1375, 1209, 1171, 1141, 724 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0.9 (t, 6H, J = 6.6 Hz, 2 x (CH_3-CH_2-)), 1.2-1.8 (m, 26H, (CH_3-$(CH_2)_5$-CH(CH_3)-Se)$_2$), 3.0-3.1 (m, 2H, (-CH-Se)$_2$).. ^{77}Se-NMR ($CDCl_3$) δ = 374.4 and 374.6. Mass spectrum 386 (M), 274 (CH_3-$(CH_2)_5$-CH(CH_3)-SeSeH), 193 (CH_3-$(CH_2)_5$-CH(CH_3)-Se), 113 (CH_3-$(CH_2)_9$-CH(CH_3)), 71 (CH_3-$(CH_2)_4$), 57 (CH_3-$(CH_2)_3$).

Di(5-chloro-pentyl) diselenide (52 %, as an oil) is prepared according to the general procedure B. 5-Chloro-pentyl selenocyanate (421 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (60 mg, 80 % in 1 ml DMF). The resulting mixture is stirred at 20°C for 5 h, then treated. R_f 0.38 (ether/pentane: 2/8). IR (neat) 2930, 2856, 1457, 1452, 1301, 1281, 1230, 1198, 722, 651 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 1.5-1.7 (m, 4H, 2 x (-CH_2-CH_2-CH_2-Cl), 1.7-1.9 (m, 8H, 2 x (-CH_2-CH_2-CH_2-CH_2-Cl)), 2.91 (t, 4H, J = 7.3 Hz, (-CH_2-Se)$_2$), 3.54 (t, 4H, J = 6.6 Hz, 2 x (-CH_2-Cl)). ^{77}Se-NMR ($CDCl_3$) δ = 309.

Di(5-cyano-pentyl) diselenide (67 %, as an oil) is prepared according to the general procedure B. 5-bromo-pentyl selenocyanate (510 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (60 mg, 80 % in 1 ml DMF). The resulting mixture is stirred at 20°C for 5 h, then treated. R_f 0.41 (ether/pentane: 2/8). IR (neat) 2932, 2858, 2245, 1456, 1423, 1266, 1240, 1211, 1176, 721 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 1.4-2 (m, 12H, 2 x (-CH_2-(CH_2)$_3$-CH_2-)), 2.37 (t, 4H, J =

6.3 Hz, 2 x (-C$\underline{H}_2$-CN)), 2.91 (t, 4H, J = 6.9 Hz, (-C$\underline{H}_2$-Se)$_2$). ^{77}Se-NMR ($CDCl_3$) δ = 308. Mass spectrum 352 (M), 257 (M - HCN - (NC-CH_2-$(CH_2)_3$)), 176 (Se-$(CH_2)_5$-CN).

Di(methyl 4-butanoate) diselenide (60 %, as an oil) is prepared according to the general procedure B. Methyl 4-selenocyanatobutanoate (512 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (60 mg, 80 % in 1 ml DMF). The resulting mixture is stirred at 20°C for 1.5 h, then treated. Rf 0.53 (pentane/ether : 5/5). IR (neat) 3448, 2991, 2949, 2846, 1733, 1653, 1647, 1636, 1628, 1559, 1541, 1507, 1437, 1363, 1300, 1203, 1125, 1053, 1019, 986, 951, 931,886, 852, 812, 771, 753 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 2.0-2.15 (m, 4H, 2 x (CH_2-C$\underline{H}_2$-CH_2), 2.45 (t, 4H, J = 7.1 Hz, 2 x (-C$\underline{H}_2$-C=O)), 2.9 (t, 4H, J = 7.3 Hz, (-C$\underline{H}_2$-Se)$_2$), 3.68 (s, 6H, 2 x (CH_3-O-)). ^{77}Se-NMR ($CDCl_3$) δ = 302. Mass spectrum 362 (M), 181 (CH_3-O-CO-$(CH_2)_3$-Se), 59 (CH_3-O-C=O). Analysis for $C_{10}H_{18}O_4Se_2$: calculated (C 33.35; H 5.04 %), found (C 33.47; H 5.05 %).

Benzyl phenyl selenide (66 %, as an oil) is prepared according to the general procedure C. Phenyl selenocyanate (364 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (130 mg, 80 % in 1 ml DMF). The resulting mixture is stirred for 0.5 h at 75°C, then the benzyl bromide is added. R_f=0,38 (pentane). IR (neat) 3063, 3030, 2926, 2855, 1948, 1891, 1814, 1717, 1658, 1601, 1573, 1495, 1477, 1454, 1438, 1411, 1375, 1312, 1227, 1202, 1116, 1073, 1023, 757, 737, 606 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 4.04 (s, 2H, C_6H_5-C$\underline{H}_2$-Se), 7.05-7.5 (2m, 10H, $C_6\underline{H}_5$-CH_2-Se-$C_6\underline{H}_5$). ^{77}Se-NMR ($CDCl_3$) δ = 375. Mass spectrum 248 (M), 185, 157 (M-$PhCH_2$), 91($PhCH_2$).

Benzyl *n*-butyl selenide (75 %, as an oil) is prepared according to the general procedure C. The *n*-butyl selenocyanate (324 mg, 2 mmol in 0,5 ml DMF) is added to the suspension of NaH (130 mg, 80 % in 0,5 ml DMF). The resulting mixture is stirred for 0,3 h at 75°C, then the benzyl bromide is added. Rf 0.36 (pentane). IR (neat) 3060, 3025, 2955, 2870, 1940, 1600, 1493, 1463, 1453, 1377, 1258, 1181, 1067, 1023, 909, 757, 696, 666 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0.88 (t, 3H, J = 7.33 Hz, C$\underline{H}_3$), 1.3-1.45 (m, 2H, CH_3-C$\underline{H}_2$), 1.5-1.7 (m, 2H, C$\underline{H}_2$-CH_2-Se), 2.48 (t, 2H, J = 7.55 Hz, C$\underline{H}_2$-Se) 3.67 (s, 2H, C_6H_5-C$\underline{H}_2$-Se), 7.1-7.4 (m, 5H, $C_6\underline{H}_5$-CH_2-Se). ^{77}Se-NMR ($CDCl_3$) δ = 254. Mass spectrum 214 (M-CH_2), 117, 91 ($PhCH_2$), 65. Analysis for $C_{11}H_{16}Se$: calculated (C 59.15; H 7.10 %), found (C 58.95; H 7.11 %).

Benzyl *n*-decyl selenide (70 %, as an oil) is prepared according to the general procedure C. *n*-Decyl selenocyanate (492 mg, 2 mmol in 0.5 ml DMF) is added to the suspension of NaH (130 mg, 80 % in 0.5 ml DMF). The resulting mixture is stirred at 75°C for 0.5 h, then the benzyl bromide is added. R_f 0.49 (pentane). IR (neat) 3081, 3060, 3025, 2923, 2852, 1938, 1869, 1795, 1717, 1653, 1599, 1592, 1493, 1376, 1332, 1299, 1266, 1240, 1240, 1215, 1182, 1029, 786, 757, 696, 626, 610 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 0.88 (t, 3H, J = 6.84, C$\underline{H}_3$), 1.2-1.4 (m, 14H, CH_3-$(C\underline{H}_2)_7$), 1.55-1.65 (m, 2H, C$\underline{H}_2$-CH_2-Se), 2.46 (t, 2H, J = 7.4 Hz, C$\underline{H}_2$-Se), 3.75 (s, 2H, C_6H_5-C$\underline{H}_2$-Se), 7.1-7.3 (m, 5H, $C_6\underline{H}_5$-CH_2). ^{77}Se-NMR ($CDCl_3$) δ = 254. Mass spectrum 312 (M), 257 (M- $PhCH_2$), 91 ($PhCH_2$). Analysis for $C_{17}H_{28}Se$: calculated (C 65.58; H 9.06 %), found (C 65.41; H 9.01 %).

Benzyl isopropyl selenide (50 %, as an oil) is prepared according to the general procedure C. Isopropyl selenocyanate (296 mg, 2 mmol in 1 ml DMF) is added to the suspension of NaH (130 mg, 80 % in 1 ml DMF). The resulting mixture is stirred for 0,5 h at 75°C, then the benzyl bromide is added. R_f 0.69 (pentane). IR (neat) 3083, 3062, 2954, 2920, 2862, 1945, 1873, 1806, 1601, 1494, 1453, 1382, 1367, 1314, 1221, 1183, 1155, 1066, 1030, 910, 879, 925, 757, 697, 629, 611 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ = 1.4 (d, 6H, J = 6.9, $(C\underline{H}_3)_2$-CH), 3.0-3.1 (m, 1H, C$\underline{H}$-Se), 3.8 (s, 2H, C_6H_5-C$\underline{H}_2$-Se), 7.1-7.4 (m, 5H, $C_6\underline{H}_5$). ^{77}Se-NMR ($CDCl_3$) δ = 376. Mass spectrum 214 (M), 91 ($PhCH_2$), 65. Analysis for $C_{10}H_{14}Se$: calculated (C 56.34; H 6.62 %), found (C 56.28; H 6.70 %)

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(*Received* 17 *March* 1997; *accepted* 29 *April* 1997)