Typical recovery of reaction products:[12] compound **4** (0.350 g, 0.514 mmol) was dissolved in CH_3OH/CH_3CN (1:1) and kept standing for a few weeks at room temperature. The green crystals which separated from the reaction mixture were collected, and the brown filtrate was evaporated in vacuo. The residue was dissolved in concentrated aqueous NH_3 (10 mL) and extracted with $CHCl_3$ (4×10 mL). The combined organic fractions were washed with concentrated aqueous NaCl (3×10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to leave a brown oil. Compounds **2** and **3** were separated by column chromatography, and their structures and yields were determined by ^{1}H NMR. The structure of ligand HL′ in **5** was determined by X-ray analysis of **5** and by ^{1}H NMR after removal of Cu^{II} as described above. Compound **2**: Yield, 15 %; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.33$ (s, 9H; $(CH_3)_3C$), 1.43 (s, 9H; $(CH_3)_3C$), 7.34 (d, 1H; phenol-H), 7.59 (d, 1H; phenol-H), 9.87 (s, 1H; phenol-OH), 11.64 (s, 1H; CHO). Compound **3**: Yield, 15 %; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (s, 9H; $(CH_3)_3C$), 1.43 (s, 9H; $(CH_3)_3C$), 3.93 (s, 2H; CH_2), 3.98 (s, 2H; CH_2), 6.84 (d, 2H; phenol-H), 7.2 (m, 3H; py-H, phenol-H), 7.66 (td, 1H; py-H), 8.58 (d, 1H; py-H). Compound **5**: Yield, 12 %; elemental analysis (%) calcd for $C_{35}H_{50}N_2O_2CuCl_2$: C 63.19, H 7.58, N 4.21; found: C 63.07, H 7.532, N 4.27. HL′: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.11$ (s, 9H, $(CH_3)_3C$), 1.33 (s, 9H, $(CH_3)_3C$), 1.37 (s, 9H, $(CH_3)_3C$), 1.47 (s, 9H, $(CH_3)_3C$), 3.47 (q, 2H; CH_2), 3.73 (q, 2H; CH_2), 6.27 (d, 1H; phenol-H), 6.90 (d, 1H; phenol-H), 7.14 (dd, 1H; py-H), 7.16 (d, 1H; phenol-H), 7.19 (d, 1H; py-H), 7.37 (d, 1H; phenol-H), 7.60 (td, 1H; py-H), 8.52 (d, 1H; py-H).

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[9] X-ray crystal structure determination: The X-ray diffraction data were collected at 295 K with a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). Crystal data for **1**: Formula $C_{76}H_{108}N_4O_9Cu_2$, $M_w = 1348.80$, crystal size: $0.3 \times 0.1 \times 0.1$ mm, monoclinic, space group $P2_1/n$, $a = 26.782(4)$, $b = 10.672(2)$, $c = 26.819(3)$ Å, $\beta = 94.33(1)°$, $V = 7643(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.352$ g cm^{-3}, $\mu = 12.39$ cm^{-1}, $F(000) = 3112.00$, 13682 independent reflections, 8230 reflections used, 821 parameters, $R = 0.074$, $R_w = 0.085$ ($I > 2.00\sigma(I)$). In the asymmetric unit there were two crystallographically independent complex molecules, which have very similar structures and may be regarded as mirror images arising from the coordination of the tertiary amine nitrogen to Cu^{II}. Crystal data for **4**: Formula $C_{37}H_{56}N_2O_3Cl_2Cu$, $M_w = 711.31$, crystal size: $0.17 \times 0.10 \times 0.06$ mm, triclinic, space group $P\bar{1}$, $a = 13.865(4)$, $b = 16.048(5)$, $c = 10.378(5)$ Å, $\alpha = 98.69(5)$, $\beta = 104.67(4)$, $\gamma = 112.64(2)°$, $V = 1980(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.193$ g cm^{-3}, $\mu = 22.80$ cm^{-1}, $F(000) = 758.00$, 5791 independent reflections, 5791 reflections used, 407 parameters, $R = 0.083$, $R_w = 0.128$ ($I > 2.00\sigma(I)$). Crystal data for **5**: Formula $C_{35}H_{50}N_2O_2Cl_2Cu$, $M_w = 665.24$, crystal size: $0.20 \times 0.15 \times 0.03$ mm, monoclinic, space group $P2_1/a$, $a = 18.054(4)$, $b = 12.712(7)$, $c = 18.314(4)$ Å, $\beta = 116.00(1)°$, $V = 3783(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.168$ g cm^{-3}, $\mu = 23.35$ cm^{-1}, $F(000) = 2256.00$, 5357 independent reflections, 4926 reflections used, 380 parameters, $R = 0.069$, $R_w = 0.107$ ($I > 2.00\sigma(I)$). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-136595, -136596, and -136821. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)..

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Reaction of Organic Selenocyanates with Hydroxides: The One-Pot Synthesis of Dialkyl Diselenides from Alkyl Bromides

Alain Krief,* Willy Dumont, and Cathy Delmotte

Dedicated to Professor Bernd Giese
on the occasion of his 60th birthday

Since the beginning of organoselenium chemistry, organoselenocyanates have occupied a privileged position.[1] They are easily prepared, are stable to atmospheric conditions, and have widely contributed to the use of organoselenium compounds in synthesis due to their exceptional versatility.[1] They react with a large variety of compounds, producing chemoselectively, in a single step and in almost quantitative

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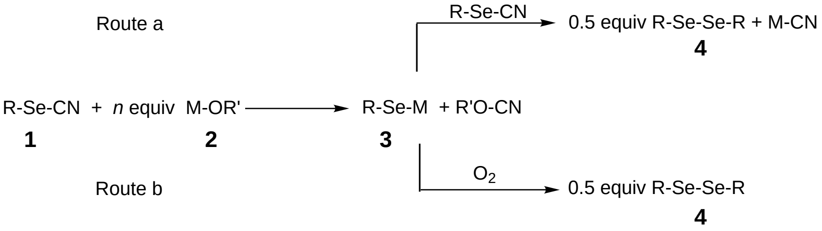
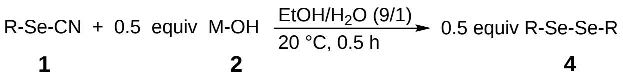
yields, selenolates ($NaBH_4$,[2a–d, 3c,d] SmI_2,[2e–g] Bu_4NF,[2g]), diselenides ($NaBH_4$, MH),[3] selenols (H_3PO_2),[4] selenenyl halides or trihalides (halogens)[5] as well as organic selenides (alcohols and Bu_3P,[1f,g, 6] organometallic compounds[7]).

The reaction of organoselenocyanates with hydroxides[8] and alkoxides[9] has been documented over the last 110 years, but the results lack consistency since, depending upon the case, either selenolates **3** [8a–c] or diselenides **4** are produced[8d–k, 9] (Scheme 1). It is furthermore impossible to determine if the diselenides **4** are directly formed (route a)[8d–f] or if they result from oxidation of the initially formed selenolates **3**, fortuitously by air during or after the reaction[8g–i] or intentionally by bubbling of oxygen through the medium[8j,k] (route b). Although both conditions produce the diselenides **4**, the amount of reagent **2** required would be different (0.5 equiv for route a and 1 equiv for route b) as are the nature and amount of the by-products formed (0.5 equiv each of HOCN and MCN for route a and 1 equiv of HOCN for route b).



Scheme 1. Reaction of organic selenocyanates with alkaline hydroxides and alkoxides. $n = 0.5$ (route a), 1 (route b); R = Ar, Alk, R′ = Me, Et, M = Na, K.



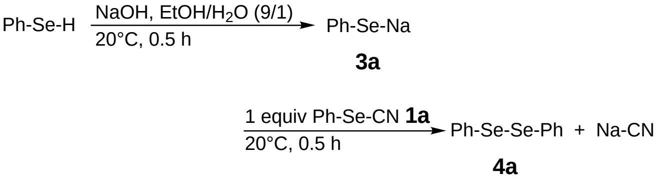
$$\underset{\mathbf{1}}{\text{R-Se-CN}} + 0.5\ \text{equiv}\ \underset{\mathbf{2}}{\text{M-OH}} \xrightarrow[20\ ^\circ\text{C},\ 0.5\ \text{h}]{\text{EtOH/H}_2\text{O (9/1)}} 0.5\ \text{equiv}\ \underset{\mathbf{4}}{\text{R-Se-Se-R}}$$

The experimental conditions have not always been properly achieved and/or described. In some cases oxygen had been improperly used because the diselenide was already in the reaction medium, and oxidation of the presumed selenolate was useless. It is therefore surprising that the statement of Paulmier in his 1986 review article that "Alkaline hydrolysis of selenocyanates has never been clearly explained"[10] has not attracted much attention.

We report here our results in this field which clearly delineate the scope and limitations of the reactions involving hydroxides and phenyl or alkyl selenocyanates (see the Experimental Section). The reactions were carried out with different amounts of reagent since formally one equivalent of hydroxide is required for the synthesis of the selenolate, whereas only 0.5 equiv is needed to produce the diselenide. It was not clear at that stage if the use of 0.5 equiv of hydroxide would produce 0.5 equiv of the selenolate besides unchanged selenocyanate or if the former would react with the latter to produce the diselenide.

To clarify this point we treated sodium phenylselenolate (**3a**) with one molar equivalent of phenyl selenocyanate (**1a**) in ethanol/water (9/1) at 20 °C. The corresponding diphenyl diselenide (**4a**) was produced in 93 % yield (Scheme 2). Successful formation of a selenolate would therefore require not only that at least an equimolecular amount of hydroxide is used, but also that the hydroxide reacts faster than the resulting selenolate with the selenocyanate.[11]

We allowed selenocyanates **1** to react with 0.5 equiv of metal hydroxide in ethanol/water and found that they produce under mild conditions (20 °C, 0.5 h) the corresponding diselenides **4** in very high yields (82 – 97 %, Table 1).[11, 12] We ascertained the presence of sodium cyanide in the reaction mixture from butyl selenocyanate and NaOH (entry 2) by ^{13}C NMR spectroscopy ($\delta = 165$) and quantified its amount (0.5 equiv).[13]



Scheme 2. Synthesis of sodium phenylselenolate (**3a**) and subsequent reaction with phenyl selenocyanate (**1a**).

Table 1. Reaction of organic selenocyanates with 0.5 equiv of alkaline hydroxide.

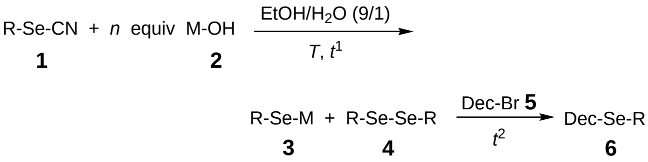
Entry	R	1	Hydroxide	Product (yield [%])
1	Ph	**1a**	KOH	**4a** (90)
2	Ph	**1a**	NaOH	**4a** (86)
3	Ph	**1a**	LiOH	**4a** (85)
4	Bu	**1b**	KOH	**4b** (97)
5	Bu	**1b**	NaOH	**4b** (82)
6	Bu	**1b**	LiOH	**4b** (96)
7	*i*Pr	**1c**	NaOH	**4c** (82)

We also observed that the reactions carried out with one or more equivalents of hydroxide provide, depending upon the nature of the selenocyanate, either selenolates (from **1a** (Table 2, entries 1 – 3), often contaminated with **4a**) or

Table 2. Reaction of organic selenocyanates with at least one equivalent of alkaline hydroxide.

Entry	R	1	*n*	Hydroxide	*T* [°C]	t^1 [h]	t^2 [h]	Yield of **4** [%]	Yield of **6** [%]	Recovered **5** [%]
1	Ph	**1a**	1	KOH	20	1	20	29	70	29
2	Ph	**1a**	1	NaOH	20	0.5	20	0	90	0
3	Ph	**1a**	1	LiOH	80	2	19	35	41	57
4	Bu	**1b**	5	KOH	80	2	2	71	14	53
5	Bu	**1b**	5	NaOH	80	3	2	74	14	82
6	*i*Pr	**1c**	1	NaOH	80	1	20	80	5	77
7	$PhCH_2$	**1d**	5	KOH	20	0.5	23	75	9	64

diselenides (from alkyl selenocyanates **1b–d**; entries 4–7). Quenching the reactions with *n*-decyl bromide (Dec–Br, **5**) leads to decyl phenyl selenide (**6a**) as the major compound for reaction of **1a** and alkyl decyl selenides **6b–d** in trace amounts for reactions of **1b–d**, confirming the results just described.

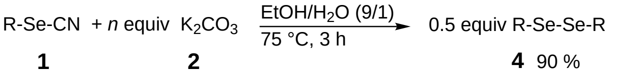


$$\underset{\mathbf{1}}{\text{R-Se-CN}} + n\text{ equiv }\underset{\mathbf{2}}{\text{M-OH}} \xrightarrow[T,\,t^1]{\text{EtOH/H}_2\text{O (9/1)}} \underset{\mathbf{3}}{\text{R-Se-M}} + \underset{\mathbf{4}}{\text{R-Se-Se-R}} \xrightarrow[t^2]{\text{Dec-Br }\mathbf{5}} \underset{\mathbf{6}}{\text{Dec-Se-R}}$$

Sodium hydroxide proved to be the most effective reagent for the synthesis of phenyl selenolate (**3a**; Table 2, entry 2). The lower yields observed when potassium or lithium hydroxide was used could be due to the poor solubility of the former under the standard conditions (entry 1) and the poorer nucleophilicity of the latter (entry 3). Both KOH and LiOH favor the competing reaction of **3a** with **1a**, which leads to diphenyl diselenide (**4a**, Table 1, entry 1).

We have proved in separate experiments that reactions of **1a** and NaOH (0.5 equiv; EtOH/H_2O (90/10), 20°C, 2 h) carried out under a flow of oxygen delivered diphenyl diselenide **4a** (87%) and dibutyl diselenide **4b** (83%) in yields similar to those obtained for the reaction under argon. These results clearly show that the selenolate intermediate reacts more rapidly with the selenocyanate than with oxygen, otherwise some selenocyanate (up to 50%) would have been left and this proved not to be the case.[14]

We have also found that potassium carbonate in aqueous ethanol reacts with selenocyanates, regardless of their nature (alkyl or aryl), to produce the corresponding diselenides **4** (Scheme 3).[11, 15] The reaction already occurs at 20°C, but is particularly slow for butyl selenocyanate (**1b**); dibutyl diselenide (**4b**) is obtained besides recovered starting material (0.25 equiv K_2CO_3, 72 h, **4b**:**1b** = 52:48; 1 equiv K_2CO_3, 72 h, **4b**:**1b** = 76:24). The reaction is faster with phenyl selenocyanate (**1a**) and leads almost exclusively to diphenyl diselenide (**4a**) when carried out with an excess of potassium carbonate (1 equiv K_2CO_3, 20°C, 20 h, 75% yield of isolated product). However, the best results were obtained in both series by performing the reaction at 75°C (0.25–1 equiv K_2CO_3, 3 h, **4** isolated in 80–85% yield).

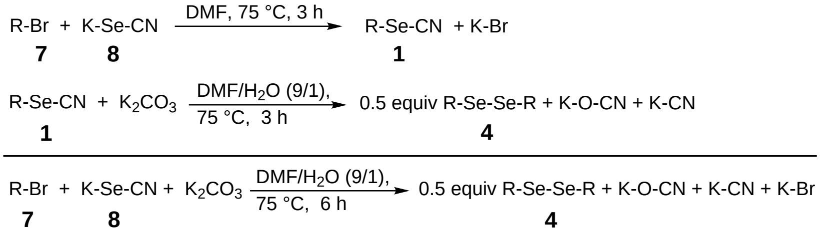


$$\underset{\mathbf{1}}{\text{R-Se-CN}} + n\text{ equiv }\underset{\mathbf{2}}{K_2CO_3} \xrightarrow[75\,^{\circ}\text{C, 3 h}]{\text{EtOH/H}_2\text{O (9/1)}} 0.5\text{ equiv }\underset{\mathbf{4}\ 90\,\%}{\text{R-Se-Se-R}}$$

Scheme 3. Reaction of organic selenocyanates with potassium carbonate. The conditions found to be the best are given; see text for details. R = Ph, *n*Bu.

Taking advantage of the observations made during this work, we designed a very mild, one-pot synthesis of dialkyl diselenides from alkyl bromides, potassium selenocyanate, and potassium carbonate (Scheme 4; 1 equiv of each reagent; **4b**: 71%, **4d**: 83%; **4** (R = 2-pentyl): 80%). These reactions were performed in DMF rather than ethanol because the former is the best medium for the synthesis of alkyl selenocyanates.[3c,d] Furthermore, although only 0.25 equiv of potassium carbonate is required, we carried out the reactions with an excess of this reagent because they are otherwise too slow.

Although efficient, this reaction releases potassium cyanide (0.5 equiv). A slight modification of the synthetic scheme—which takes into account that potassium cyanide reacts with elemental selenium to produce potassium selenocyanate[1] and that 0.5 equiv of cyanide is generated in the reaction of the butylselenolate with butyl selenocyanate—allows the one-pot synthesis of dibutyl diselenide (**4b**) from *n*-butyl bromide, elemental selenium (1 equiv), potassium cyanide (0.5 equiv), and potassium carbonate (1 equiv; Scheme 5). This reaction compares well with the one-pot synthesis of organic selenocyanates described by Chandrasekaran and Prabhu,[16] which also uses elemental selenium as the starting material.

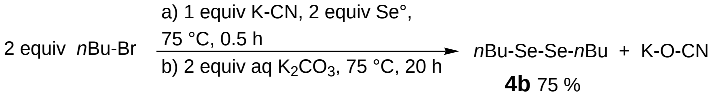


$$\underset{\mathbf{7}}{\text{R-Br}} + \underset{\mathbf{8}}{\text{K-Se-CN}} \xrightarrow{\text{DMF, 75 °C, 3 h}} \underset{\mathbf{1}}{\text{R-Se-CN}} + \text{K-Br}$$

$$\underset{\mathbf{1}}{\text{R-Se-CN}} + K_2CO_3 \xrightarrow[75\,^{\circ}\text{C, 3 h}]{\text{DMF/H}_2\text{O (9/1),}} 0.5\text{ equiv }\underset{\mathbf{4}}{\text{R-Se-Se-R}} + \text{K-O-CN} + \text{K-CN}$$

$$\underset{\mathbf{7}}{\text{R-Br}} + \underset{\mathbf{8}}{\text{K-Se-CN}} + K_2CO_3 \xrightarrow[75\,^{\circ}\text{C, 6 h}]{\text{DMF/H}_2\text{O (9/1),}} 0.5\text{ equiv }\underset{\mathbf{4}}{\text{R-Se-Se-R}} + \text{K-O-CN} + \text{K-CN} + \text{K-Br}$$

Scheme 4. Sequential reaction of alkyl bromides with potassium selenocyanate and potassium carbonate.



$$2\text{ equiv }n\text{Bu-Br} \xrightarrow[\text{b) 2 equiv aq K}_2\text{CO}_3\text{, 75 °C, 20 h}]{\text{a) 1 equiv K-CN, 2 equiv Se°, 75 °C, 0.5 h}} \underset{\mathbf{4b}\ 75\,\%}{n\text{Bu-Se-Se-}n\text{Bu}} + \text{K-O-CN}$$

Scheme 5. One-pot reaction of *n*-butyl bromide with elemental selenium, potassium cyanide, and potassium carbonate.

In conclusion we have described the scope, limitations, and important mechanistic details of the reaction of organic selenocyanates with hydroxides, an old reaction which was not properly understood. We have found that it is particularly efficient for the synthesis of diselenides and that potassium carbonate is an even milder reagent for that purpose.

Experimental Section

General: The reactions of hydroxide and phenyl or alkyl selenocyanate were carried out in aqueous ethanol (as previously used)[4, 6, 7] under different experimental conditions. Care was taken to avoid oxidation of the selenolate, if formed, by conducting the reactions under argon and quenching, at least once for each set of reactions, with *n*-decyl bromide (**5**) to produce decyl phenyl selenide (**6a**) or alkyl decyl selenides **6b**, **c** (see Table 2). The selenide and/or the diselenide were isolated and in some cases their ratio was corroborated by gas chromatography (GC) using an internal standard or by ^1H NMR spectroscopy.

Synthesis of **4** from **1** and metal hydroxide (0.5 equiv): The organic selenocyanate **1** (2 mmol) and ethanol (5 mL) were placed in a 25-mL, two-necked flask fitted with a magnetic stirrer, a septum, and an argon-filled balloon. The hydroxide (1 mmol in 0.25 mL of water) was introduced by syringe. The resulting mixture was stirred at 20 °C for 0.5 h and then hydrolyzed (10 mL of water) and extracted with diethyl ether (2 × 20 mL). The ether fractions were combined, washed with water (2 × 20 mL), and dried over MgSO$_4$. The solvent was evaporated in vacuo. The crude mixture was fractionated by column chromatography on silica gel using pentane as eluent.

Synthesis of **6a** from **1a** and NaOH (1 equiv): Phenyl selenocyanate (**1a**, 2 mmol) and ethanol (5 mL) were introduced into a 25-mL, two-necked flask fitted with a magnetic stirrer, a septum, and an argon-filled balloon. Sodium hydroxide (2 mmol in 0.5 mL of water) was added by syringe. The resulting mixture was stirred for 2 h at 20 °C. *n*-Decyl bromide (**5**, 2 mmol in 1 mL of ethanol) was added. The mixture was stirred for 20 h at 20 °C and then hydrolyzed (10 mL of water) and extracted with diethyl ether (2 × 20 mL). The ether fractions were combined, washed with water (2 × 20 mL), and dried over MgSO$_4$. The solvent was evaporated in vacuo. The crude mixture was fractionated by column chromatography on silica gel using pentane as eluent to provide **6a** in 90 % yield.

One-pot synthesis of **4b** from *n*-butyl bromide and potassium selenocyanate: KSeCN (2 mmol) and DMF (2 mL) were introduced into a 25-mL, two-necked flask fitted with a magnetic stirrer, a septum, and a condenser connected to an argon-filled balloon. The solution was heated to 75 °C, and *n*BuBr (2 mmol in 1 mL of DMF) was added. The resulting mixture was stirred for 3 h at 75 °C. K$_2$CO$_3$ (2 mmol in 0.8 mL of water) was slowly introduced by syringe. The resulting mixture was stirred for 3 h at 75 °C and then hydrolyzed (10 mL of water) and extracted with diethyl ether (2 × 20 mL). The ether fractions were combined, washed with water (2 × 20 mL), and dried over MgSO$_4$. The solvent was evaporated in vacuo. The crude mixture was fractionated by column chromatography on silica gel using pentane as eluent to provide **4b** in 71 % yield.

One-pot synthesis of **4b** from *n*-butyl bromide and elemental selenium. KCN (1 mmol) and DMF (3 mL) were introduced into a 25-mL, two-necked flask fitted with a magnetic stirrer, a septum, and a condenser connected to an argon-filled balloon. The solution was heated to 75 °C. Elemental selenium (2 mmol) was added and the mixture stirred for 0.25 h at 75 °C. Then *n*BuBr (2 mmol in 1 mL of DMF) and K$_2$CO$_3$ (2 mmol in 0.5 mL of water) were introduced. The resulting mixture was stirred for 20 h at 75 °C and then hydrolyzed (10 mL of water) and extracted with diethyl ether (2 × 20 mL). The ether fractions were combined, washed with water (2 × 20 mL), and dried over MgSO$_4$. The solvent was evaporated in vacuo. The crude mixture was fractionated by column chromatography on silica gel using pentane as eluent to provide **4b** in 75 % yield.

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[11] The reaction proceeds similarly if carried out in DMF instead.

[12] We have demonstrated that ethanol does not react with selenocyanates.

[13] Merck Cyanid Test reference No. 1.10044–0001 (Merck, Darmstadt, Germany).

[14] The same reactions have been carried out with one equivalent of NaOH and also provide the corresponding diselenides.

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