

Typical recovery of reaction products:^[12] compound **4** (0.350 g, 0.514 mmol) was dissolved in CH₃OH/CH₃CN (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 NH₃ (10 mL) and extracted with CHCl₃ (4 × 10 mL). The combined organic fractions were washed with concentrated aqueous NaCl (3 × 10 mL), dried over Na₂SO₄, 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 ¹H NMR. The structure of ligand HL' in **5** was determined by X-ray analysis of **5** and by ¹H NMR after removal of Cu^{II} as described above. Compound **2**: Yield, 15%; ¹H NMR (300 MHz, CDCl₃): δ = 1.33 (s, 9H; (CH₃)₃C), 1.43 (s, 9H; (CH₃)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%; ¹H NMR (300 MHz, CDCl₃): δ = 1.28 (s, 9H; (CH₃)₃C), 1.43 (s, 9H; (CH₃)₃C), 3.93 (s, 2H; CH₂), 3.98 (s, 2H; CH₂), 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 C₃₅H₅₀N₂O₂CuCl₂: C 63.19, H 7.58, N 4.21; found: C 63.07, H 7.532, N 4.27. HL': ¹H NMR (300 MHz, CDCl₃): δ = 1.11 (s, 9H; (CH₃)₃C), 1.33 (s, 9H; (CH₃)₃C), 1.37 (s, 9H; (CH₃)₃C), 1.47 (s, 9H; (CH₃)₃C), 3.47 (q, 2H; CH₂), 3.73 (q, 2H; CH₂), 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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Reaction of Organic Selenocyanates with Hydroxides: The One-Pot Synthesis of Dialkyl Diselenides from Alkyl Bromides

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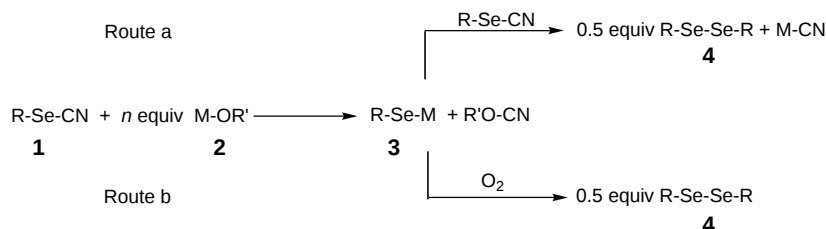
Dedicated to Professor Bernd Giese
on the occasion of his 60th birthday

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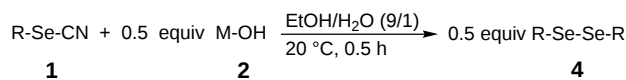
yields, selenolates (NaBH_4 ,^[2a-d, 3c,d] SmI_2 ,^[2e-g] Bu_4NF ,^[2g]), diselenides (NaBH_4 , MH),^[3] selenols (H_3PO_2),^[4] selenenyl halides or trihalides (halogens)^[5] as well as organic selenides (alcohols and Bu_3P ,^[1f,g, 6] organometallic compounds^[7]).

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



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

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).

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.

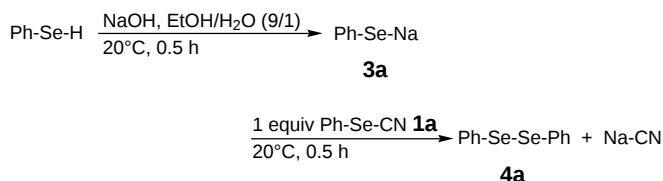
We report here our results in this field which clearly delineate the scope and limitations of the reactions involving hydroxides and phenyl or alkyl selenocyanates (see the Experimental Section). The reactions were carried out with

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>i</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 [$^\circ\text{C}$]	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>i</i> Pr	1c	1	NaOH	80	1	20	80	5	77
7	PhCH_2	1d	5	KOH	20	0.5	23	75	9	64

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 MgSO₄. 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 MgSO₄. 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. K₂CO₃ (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 MgSO₄. 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 K₂CO₃ (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 MgSO₄. 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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