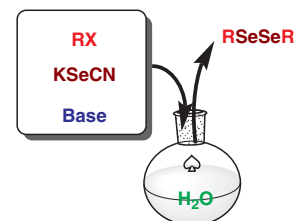


Aqueous Medium Preparation of Dialkyldiselenides

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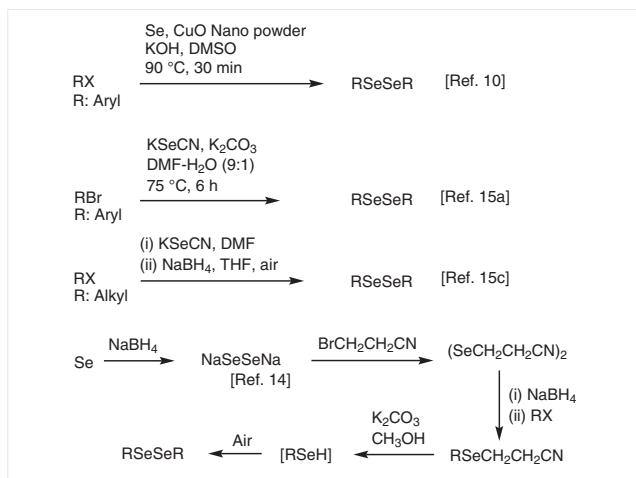
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Abstract One-pot, two-step reaction conditions have been developed for the preparation of dialkyl diselenides by the treatment of alkyl halides with potassium selenocyanate followed by alkaline hydrolysis of the in situ generated alkyl selenocyanate in water. The reaction is reasonably fast and the yields of the products were very good. Several functional groups present in the substrates were unaffected under the reaction conditions.

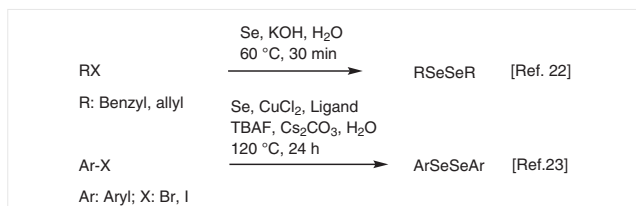
Key words selenium, alkyl halides, dimerization, sustainable chemistry, water

Organochalcogenides such as disulfides and diselenides have been used as intermediates and reagents in a wide variety of organic reactions.¹ A large number of thio- and seleno- compounds have been shown to have the potential to act as biologically active molecules² such as antioxidants, anti-ulcer and anti-inflammatory agents as well as therapeutics against cancer and various infectious diseases.³ They also play important roles in material science and nanotechnology.⁴ Given their synthetic utility, a number of reaction conditions have been developed for the preparation of diorganyl diselenide derivatives. Most of the reaction conditions for the preparation of this class of compound involve the use of metal diselenides derived from the reaction of elemental selenium or selenium oxide with a strong reducing agent such as sodium borohydride,⁵ lithium triethylborohydride,⁶ hydrazine,⁷ sodium hydride,⁸ SmI₂,⁹ metal oxide nanoparticles,¹⁰ carbon monoxide,¹¹ and under alkaline phase transfer conditions.¹² They have furthermore

been prepared by the oxidation of selenols or selenoates.¹³ Diselenides have also been prepared through the formation a di-2-cyanoethyl diselenide derivative and its reaction with alkyl halides.¹⁴ In another approach, alkyl halide and aryl halide,¹⁵ diazonium¹⁶ or diaryliodonium salts,¹⁷ respectively, have been converted into alkyl or aryl selenocyanate derivatives with a variety of reagents. Treatment of selenocyanate derivatives with a base or reducing agent leads to the formation of selenols, which undergo aerial oxidation to furnish diselenide derivatives (Scheme 1). Diselenide derivatives have also been prepared using hydrogen selenide, produced by the treatment of elemental selenium with carbon monoxide and water.¹⁸ Despite their synthetic utilities, the reported methods for the preparation of diselenide derivatives suffer from several shortcomings, which include the use of strong reducing agents, toxic gasses, hazardous reaction conditions, poor yields and extended reaction times. Although, preparation of diselenide derivatives by the treatment of alkyl or aryl selenocyanates with hydroxides has been known for some time,¹⁹ the mechanistic aspects of this transformation have only recently been discussed.¹⁵ Therefore, it is pertinent to develop sustainable reaction conditions for the synthesis of diselenide derivatives avoiding hazardous reagents and solvents.²⁰ Recently, reports have appeared describing the preparation of organoselenium derivatives using water as the reaction solvent.²¹ Soleiman-Beigi et al. reported²² the preparation of dialkyl diselenide derivatives by the reaction of alkyl halides and tosylates with elemental selenium in the presence of potassium hydroxide in water. In another report, Li et al. prepared²³ diaryl diselenides by copper-catalyzed coupling of aryl halides with elemental selenium in water (Scheme 2).

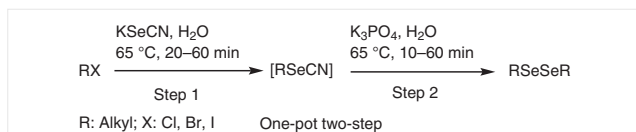


Scheme 1 Previously reported preparations of diselenides



Scheme 2 Reported methods for the preparation of diselenide derivatives under aqueous reaction conditions

However, preparation of diselenide derivatives by the treatment of alkyl halides with potassium selenocyanate (KSeCN) followed by alkaline hydrolysis of the in situ generated alkyl selenocyanate in a one-pot, two-step reaction in water has remained unexplored to date. Water is an attractive solvent for several reasons such as cost effectiveness, safety, and being environmentally benign.²⁴ In this context, a one-pot, two-step aqueous protocol is reported herein, involving treatment of alkyl halides with KSeCN followed by alkaline hydrolysis in water (Scheme 3).

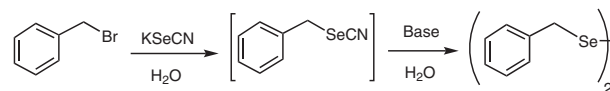


Scheme 3 Aqueous medium preparation of dialkyl diselenide derivatives from alkyl halide

In an initial set of experiments, benzyl bromide (1.0 mmol) was treated with KSeCN, ranging from 1.0–2.0 equiv in water (5 mL) at a range of temperatures. It was observed

that the use of 1.05 equiv of KSeCN in water (5 mL) at 65 °C resulted in the formation of benzyl selenocyanate in 90% yield in 30 min. After formation of the selenocyanate derivative from benzyl bromide, a diverse number of bases such as KOH, K₂CO₃, K₃PO₄, NaOH, Na₂CO₃, and Et₃N was added in excess to the reaction mixture in the same pot. It was observed that stirring the reaction mixture in the presence of K₃PO₄ at 65 °C furnished 90% dibenzyl diselenide in 30 min. Use of KOH and K₂CO₃ also resulted in the formation of the diselenide derivative in a slightly lower yield. Use of Et₃N did not give the diselenide derivative, even after 24 h (Table 1). Therefore, K₃PO₄ was selected as the best choice for hydrolysis of the selenocyanate derivative. Use of a stoichiometric quantity of K₃PO₄ did not lead to complete diselenide formation even upon extended reaction times. However, use of an excess of K₃PO₄ (5 equiv) resulted in the formation of the diselenide derivative in a reasonably short reaction time.

Table 1 Optimization of Hydrolysis of In Situ Generated Selenocyanate Derivative (Step 2) using Different Bases^a



Entry	Base	Equiv	Time (min)	Yield (%)
1	KOH	5	60	70
2	NaOH	5	60	40
3	K ₂ CO ₃	5	45	40
4	K ₃ PO ₄	5	20	90
5	K ₃ PO ₄	2	120	75
6	Na ₂ CO ₃	5	60	40
7	Et ₃ N	10	24 h	–

^a All reactions were carried out in water at 65 °C after formation of the benzyl selenocyanate from benzyl bromide by treatment with KSeCN.

A wide variety of alkyl diselenide derivatives was prepared from the corresponding halide derivatives under similar reaction conditions (Table 2). However, in the case of aliphatic and aryloxyalkyl halides, the formation of selenocyanate derivatives was relatively slow, but reaction times were significantly reduced by adding tetrabutylammonium bromide (TBAB) (0.1 mmol). In addition to simple alkyl halides, 6-deoxy-6-iodo-glycosides also furnished the corresponding diselenide derivatives under the optimized reaction conditions, although after extended reaction times. No trace of dialkyl selenide derivative was observed under these reaction conditions.²⁵

Table 2 Preparation of Diselenide Derivatives by One-Pot, Two-Step Reaction in Water

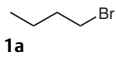
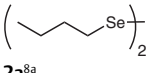

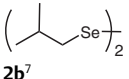

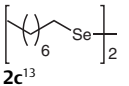

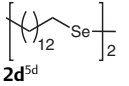
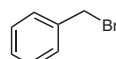
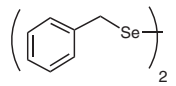
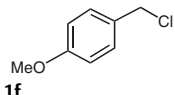
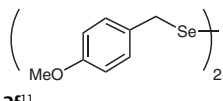
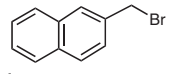
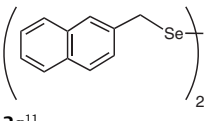
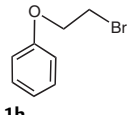
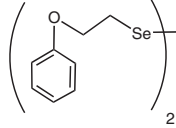
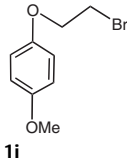
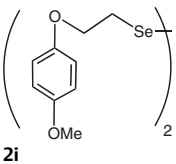
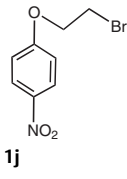
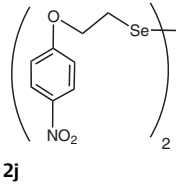
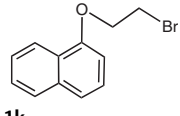
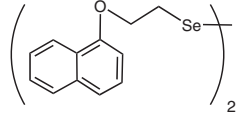
Entry	Starting material	Time (min) ^a	Product	Yield (%)
1	 1a	10 ^b (30) ^b	 2a ^{8a}	70
2	 1b	10 ^b (30) ^b	 2b ⁷	72
3	 1c	15 ^b (10) ^{b,d}	 2c ¹³	78
4	 1d	20 ^b (20) ^{b,d}	 2d ^{5d}	76
5	 1e	30 ^c (30) ^c	 2e ¹¹	90
6	 1f	240 ^c (15) ^c	 2f ¹¹	86
7	 1g	10 ^c (60) ^c	 2g ¹¹	84
8	 1h	60 ^c (45) ^{c,d}	 2h	86
9	 1i	40 ^c (30) ^{c,d}	 2i	90
10	 1j	60 ^c (60) ^{c,d}	 2j	88
11	 1k	180 ^c (150) ^c	 2k	90

Table 2 (continued)

12		10 ^c (15) ^{c,d}		76
13		15 ^c (9 h) ^{c,d}		76
14		60 ^c (8 h) ^{c,d}		75
15		15 ^c (15) ^c		80

^a Time taken in step 1 is given in parentheses.

^b Reaction carried out at room temperature.

^c Reaction carried out at 65 °C.

^d TBAB (0.1 mmol) was added.

In summary, an efficient aqueous reaction protocol has been developed for the preparation of dialkyl diselenide derivatives from the corresponding alkyl halides by a one-pot, two-step reaction.^{26,27} The yields of the products are high. This reaction protocol has several advantages over previous procedures, such as operational simplicity, sustainability, short reaction times, high yields and simple work-up.

Acknowledgment

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- (25) **General method for the preparation of dialkyl diselenides:**
To a solution of alkyl halide (1.0 mmol) in H₂O (5 mL) were added TBAB (0.1 mmol) and KSeCN (1.05 mmol) and the reaction mixture was stirred vigorously at 65 °C for the time detailed in Table 1. K₃PO₄ (5.0 mmol) was then added and the mixture was stirred at 65 °C for the time detailed in Table 2. The reaction mixture was cooled and extracted with EtOAc (2 × 25 mL), and the organic layer was dried (Na₂SO₄), filtered and concentrated. Chromatographic purification of the crude product over SiO₂ furnished pure products. Analytical data of known compounds match with the data reported in the literature.
- (26) Analytical data of novel compounds:
Di-(2-phenoxyethyl) diselenide (2h): Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 7.29–7.21 (m, 4 H, Ar-H), 6.96–6.87 (m, 6 H, Ar-H), 4.22 (t, J = 7.0 Hz, 4 H, OCH₂), 3.28 (t, J = 7.0 Hz, 4 H, SeCH₂); ¹³C NMR (125 Hz, CDCl₃): δ = 157.2–113.6 (Ar-C), 66.6 (2 C), 27.1 (2 C); ESI-MS: m/z = 402.9 [M+H]⁺; Anal. Calcd. for C₁₆H₁₈O₂Se₂ (401.96): C, 48.01; H, 4.53; found: C, 47.84; H, 4.75.
Di-(2-(4-methoxyphenoxy)ethyl) diselenide (2i): Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 6.86–6.74 (m, 8 H, Ar-H), 4.20 (t, J = 7.0 Hz, 4 H, OCH₂), 3.76 (s, 6 H, OCH₃), 3.25 (t, J = 7.0 Hz, 4 H, SeCH₂); ¹³C NMR (125 Hz, CDCl₃): δ = 153.0–113.6 (Ar-C), 67.4 (2 C), 54.5 (2 C, OCH₃), 27.2 (2 C); ESI-MS: m/z = 462.9 [M+H]⁺; Anal. Calcd. for C₁₈H₂₂O₄Se₂ (461.98): C, 46.97; H, 4.82; found: C, 46.80; H, 5.00.
Di-(2-(4-nitrophenoxy)ethyl) diselenide (2j): Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 8.22–8.17 (m, 4 H, Ar-H), 6.98–6.92 (m, 4 H, Ar-H), 4.33 (t, J = 7.0 Hz, 4 H, OCH₂), 3.30 (t, J = 7.0 Hz, 4 H, SeCH₂); ¹³C NMR (125 Hz, CDCl₃): δ = 162.0–113.4 (Ar-C), 67.3 (2 C), 26.2 (2 C); ESI-MS: m/z = 492.9 [M+H]⁺; Anal. Calcd. for C₁₆H₁₆N₂O₆Se₂ (491.93): C, 39.20; H, 3.29; found: C, 39.00; H, 3.50.
Di-(2-(2-naphthalenyloxy)ethyl) diselenide (2k): Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 7.78–7.63 (m, 6 H, Ar-H), 7.42–7.37 (m, 2 H, Ar-H), 7.32–7.30 (m, 2 H, Ar-H), 7.14–7.08 (m, 4 H, Ar-H), 4.38 (t, J = 7.0 Hz, 4 H, OCH₂), 3.36–3.31 (t, J = 7.0 Hz, 4 H, SeCH₂); ¹³C NMR (125 Hz, CDCl₃): δ = 155.2–105.9 (Ar-C), 66.7 (2 C), 27.0 (2 C); ESI-MS: m/z = 02.9 [M+H]⁺; Anal. Calcd. for C₂₄H₂₂O₂Se₂ (501.99): C, 57.61; H, 4.43; found: C, 57.45; H, 4.60.
Di-(4-(phenylthio)butyl) diselenide (2l): Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 7.31–7.13 (m, 10 H, Ar-H), 2.91 (t, J = 7.0 Hz, 4 H), 2.89 (t, J = 7.0 Hz, 4 H), 1.90–1.80 (m, 4 H), 1.79–1.71 (m, 4 H); ¹³C NMR (125 Hz, CDCl₃): δ = 135.5–124.8 (Ar-C), 32.1 (2 C), 28.8 (2 C), 28.1 (2 C), 27.8 (2 C); ESI-MS: m/z = 490.9 [M+H]⁺; Anal. Calcd. for C₂₀H₂₆S₂Se₂ (488.47): C, 49.18; H, 5.37; found: C, 49.00; H, 5.58.
- (27) **Bis-(p-methoxyphenyl 2,3,4-tri-O-benzyl-β-D-glucopyranosyl)-(6,6′)-diselenide (2m):** Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 7.32–7.19 (m, 30 H, Ar-H), 7.01 (d, J = 9.0 Hz, 4 H, Ar-H), 6.77 (d, J = 9.0 Hz, 4 H, Ar-H), 5.04 (d, J = 11.0 Hz, 2 H, PhCH), 4.92 (d, J = 11.0 Hz, 2 H, PhCH), 4.84 (d, J = 11.0 Hz, 2 H, PhCH), 4.78 (d, J = 11.0 Hz, 2 H, PhCH), 4.75 (d, J = 7.5 Hz, 2 H, H-1, H-1′), 4.73 (d, J = 11.0 Hz, 2 H, PhCH), 4.58 (d, J = 11.0 Hz, 2 H, PhCH), 3.74 (s, 6 H, OCH₃), 3.68–3.64 (m, 4 H, H-2, H-2′, H-3, H-3′), 3.62–3.57 (m, 2 H, H-5, H-5′), 3.42–3.38 (m, 2 H, H-4, H-4′), 3.37–3.34 (m, 2 H, H-6a, H-6′a), 3.12–3.06 (m, 2 H, H-6b, H-6′b); ¹³C NMR (125 Hz, CDCl₃): δ = 155.37–114.5 (Ar-C), 102.8 (2 C, C-1, C-1′), 84.4 (2 C), 82.2 (2 C), 80.8 (2 C), 75.7 (2 C, PhCH₂), 75.2 (2 C), 75.0 (2 C, PhCH₂), 74.9 (2 C, PhCH₂), 55.5 (2 C, OCH₃), 33.3 (2 C, C-6, C-6′); ESI-MS: m/z = 261.3 [M+Na]⁺; Anal. Calcd. for C₆₈H₇₀O₁₂Se₂ (1238.31): C, 66.01; H, 5.70; found: C, 65.82; H, 5.54.
Bis-(p-methoxyphenyl 2,3,4-tri-O-benzyl-β-D-galactopyranosyl)-(6,6′)-diselenide (2n): Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 7.40–7.22 (m, 30 H, Ar-H), 7.06–7.04 (m, 4 H, Ar-H), 6.77–6.74 (m, 4 H, Ar-H), 5.27 (d, J = 3.0 Hz, 2 H, H-1, H-1′), 4.93–4.47 (m, 12 H, 6 PhCH₂), 4.13–4.04 (m, 4 H, H-2, H-2′ and H-3, H-3′), 4.00–3.96 (m, 2 H, H-5, H-5′), 3.70 (br s, 6 H, 2 OCH₃), 3.66 (br s, 2 H, H-4, H-4′), 3.07–3.03 (m, 2 H, H-6a, H-6′a), 2.72–2.68 (m, 2 H, H-6b, H-6′b); ¹³C NMR (125 Hz, CDCl₃): δ = 155.2–114.5 (Ar-C), 98.3 (2 C, C-1, C-1′), 79.1 (2 C), 76.4 (2 C), 76.0 (2 C), 74.9 (2 C), 73.6 (2 C), 73.2 (2 C), 71.2 (2 C), 55.4 (2 C, OCH₃), 30.6 (2 C, C-6, C-6′); ESI-MS: m/z = 261.3 [M+Na]⁺; Anal. Calcd. for C₆₈H₇₀O₁₂Se₂ (1238.31): C, 66.01; H, 5.70; found: C, 65.80; H, 5.55.
Bis-(2,3-di-O-benzyl-β-D-propyl) diselenide (2o): Yellow oil; ¹H NMR (500 MHz, CDCl₃): δ = 7.34–7.22 (m, 20 H, Ar-H), 4.63–4.48 (m, 8 H, PhCH₂), 3.81–3.77 (m, 2 H), 3.62–3.56 (m, 4 H), 3.19–3.15 (m, 4 H); ¹³C NMR (125 Hz, CDCl₃): δ = 138.2–127.6 (Ar-C), 78.0 (2 C), 73.4 (2 C), 72.0 (2 C), 71.3 (2 C), 32.4 (2 C), 29.7 (2 C); ESI-MS: m/z = 71.1 [M+H]⁺; Anal. Calcd. for C₃₄H₃₈O₄Se₂ (670.11): C, 61.08; H, 5.73; found: C, 60.90; H, 5.95.