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A Scalable Process for the Synthesis of 1,2-Dialkyldiselanes and 1-Alkaneselenols

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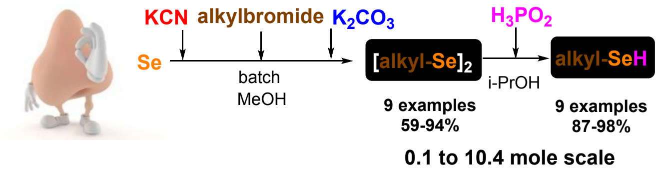
TOC Graphic


KCN
alkylbromide
K2CO3
Se
batch
MeOH
[alkyl-Se]2
9 examples
59-94%
H3PO2
i-PrOH
alkyl-SeH
9 examples
87-98%
0.1 to 10.4 mole scale

ABSTRACT

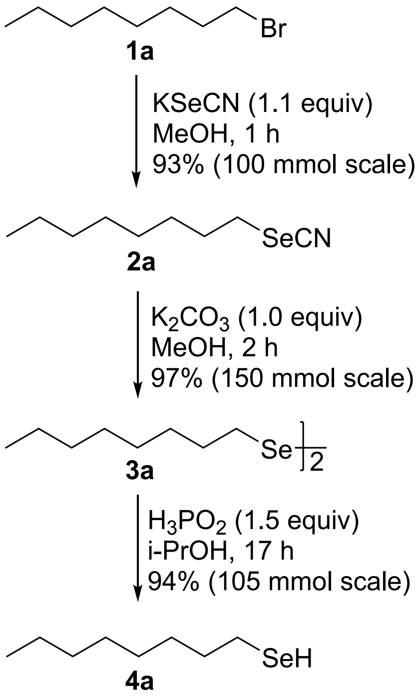
A 4-step telescoped process for the synthesis of 1-alkaneselenols entails: (1) the rapid formation of potassium selenocyanate from potassium cyanide and selenium in methanol, (2) the nucleophilic substitution of bromoalkanes or alkyl tosylates with potassium selenocyanate, (3) the mild base-catalyzed conversion of the resultant 1-alkaneseleno cyanates to 1,2-dialkyldiselanes (the Krief reaction) and (4) the reduction of the resultant 1,2-dialkyldiselanes with hypophosphorous acid to give the desired 1-alkaneselenols. The process has been used to produce 1-octaneselenol on a 10.4 mole scale. Nine examples of the process are described.

KEYWORDS

alkylselenol; dialkyldiselenol; 1-octylselenol; potassium selenocyanate; reduced odour.

INTRODUCTION

Alkaneselenols are of interest in the electronic material sector as metal selenide nanoparticles for quantum dots and surface modifiers.[1-2] We recently required a process for the synthesis of high purity 1-alkaneselenols on a kilogram scale. The overarching factors governing route selection were the need to contend with the notorious stench of lower molecular weight organoselenium compounds and the facile aerial oxidation of the target selenol compounds to their corresponding diselanes.[3] Both challenges could be addressed in principle by selecting reactions amenable to fast and easy workup. Of the many methods currently available for the synthesis of 1-alkaneselenols and their precursors,[4-11] we selected the route illustrated in Scheme 1, as exemplified by the synthesis of 1-octaneselenol (**4a**).



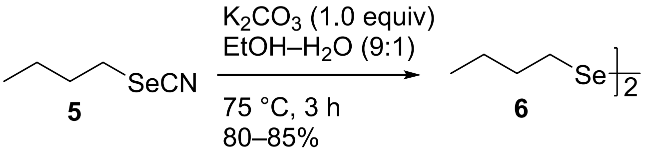
Scheme 1. The stepwise synthesis of 1-octaneselenol.

The key advantages of the component reactions are: (1) The efficient installation of the selenium atom using highly nucleophilic potassium selenocyanate,[12,13] (2) the easy isolation and purification of the 1,2-dioctyldiselane (**3a**) generated in the penultimate step and (3) the safe and efficient reduction of 1,2-dioctyldiselane (**3a**) using cheap hypophosphorous acid.

RESULTS AND DISCUSSION

The route to 1-octaneselenol (**4a**) depicted in Scheme 1 began with the addition of 1-bromooctane (1.0 equiv.) to a suspension of potassium selenocyanate (1.1 equiv., 1.0–1.5 M) in methanol. The mixture was heated at reflux for 1 h, the resultant suspension poured into ice–water and the product extracted into hexanes. The extract was washed with water, dried and concentrated in vacuo at 0 °C to give a malodorous yellow oil that was purified via short-path distillation. The principle contributors to the stench were volatile compounds that distilled at a bath temperature of ≤60 °C/1.0 mmHg into a liquid nitrogen cooled flask. When no further forerun distilled, the temperature was raised and the residual oil was collected to give 1-octaneselenocyanate (**2a**) in 93% yield as a pale yellow oil,[14] which displayed a characteristic chemical shift at δ_C = 101.7 (SeCN) and a CN stretch in the infrared spectrum at 2150 cm^{-1}.

During the course of these studies we noted the gradual formation of up to 10% of an orange-coloured, non-polar product, which was identified as 1,2-dioctyldiselane (**3a**). Since the formation of **3a** could be minimized by limiting the reaction time to 1 h and using 1.0 equiv. of potassium selenocyanate (rather than 1.1 equiv.) we reasoned that it was formed via a base-catalysed decomposition of the 1-octaneselenocyanate in the protic solvent. Krief and co-workers[15] had reported the scope, limitations and important mechanistic details of the reaction of organic selenocyanates with base and they found that it is particularly efficient for the synthesis of 1,2-dialkyldiselanes and that potassium carbonate is an especially mild reagent for that purpose, as shown in Scheme 2.



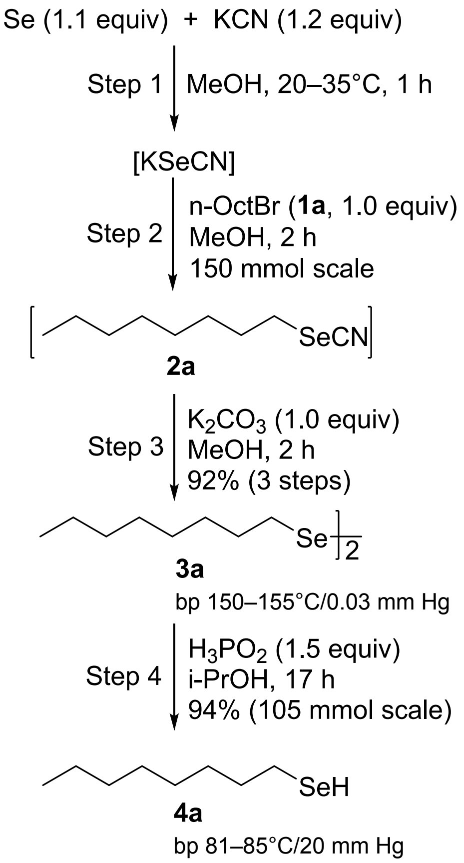
Scheme 2. The conversion of 1-butaneselenocyanate to 1,2-dibutyldiselane via the Krief reaction.

In accordance with Krief's observations, we added potassium carbonate (1.0 equiv.) to a 1.0 M solution of 1-octylselenocyanate (**2a**) in methanol. After 2 h at reflux a quantitative conversion to the 1,2-dioctyldiselane **3a** occurred in an 97% isolated yield after distillation.[16]

The final step of the sequence entailed the reduction of 1,2-dioctyldiselane (**3a**) to 1-octaneselenol (**4a**). Many reagents are known to achieve this transformation including sodium borohydride in ethanol,[17] sodium in liquid ammonia,[18] and zinc under acidic conditions.[19] On the basis of its low cost, safety and ease of workup, we selected hypophosphorous acid for development.[20] A 1.0 M solution of diselane **3a** and hypophosphorous acid was heated at reflux in 2-propanol for 17 h during which time the orange colour discharged giving a colourless solution. Removal of the solvent followed by a standard extractive workup gave 1-octaneselenol in 94% yield after distillation.[21]

Process improvements and scale-up

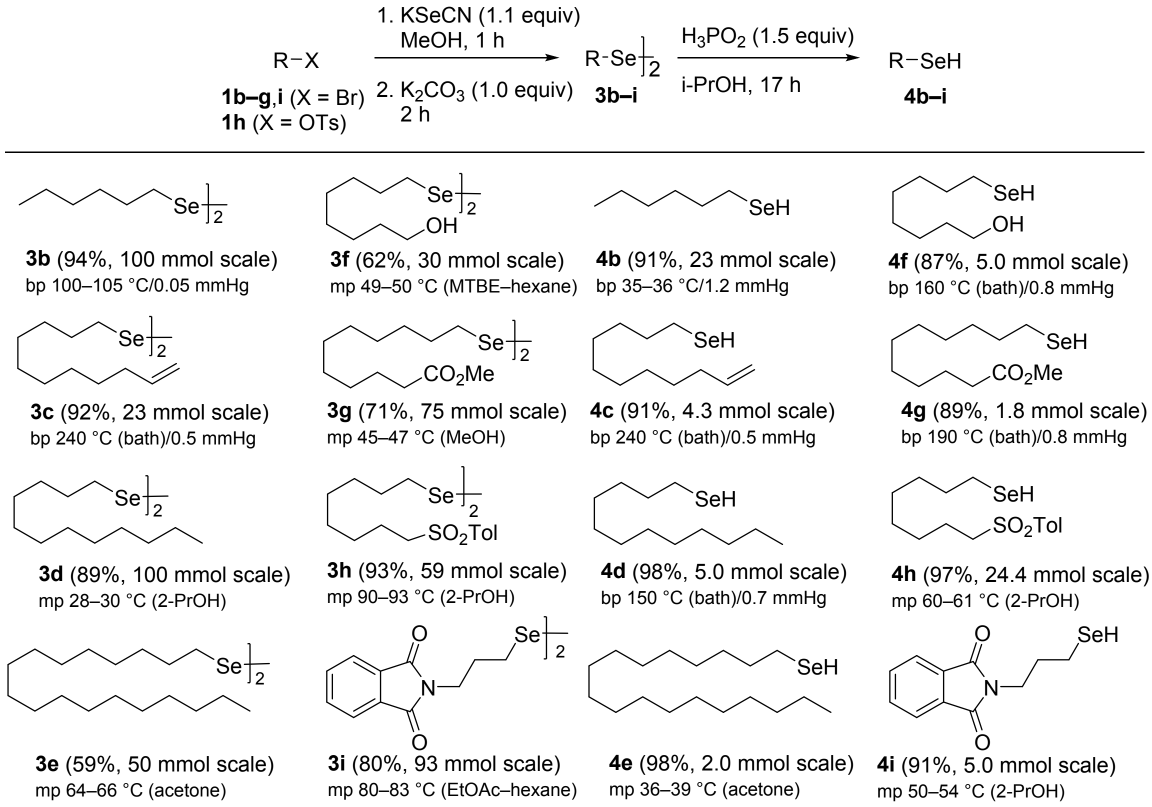
The chemistry depicted in Scheme 1 underwent three further refinements (Scheme 3). Firstly, potassium selenocyanate is commercially available but expensive. A commonly cited method for preparing it involves heating a mixture of potassium cyanide and selenium metal to a melt which is then cooled and processed.[22] We found that addition of potassium cyanide to a suspension of selenium in methanol leads to a mild exothermic reaction that is complete in 30–60 minutes giving a pale grey, turbid reaction mixture containing the potassium selenocyanate, which can be used without isolation or purification.[23] In the second refinement the succeeding two steps were telescoped; i.e., the 1-bromooctane was added to the solution of potassium selenocyanate (1.1 equiv.) and after 2 h at reflux potassium carbonate (1.0 equiv.) was added and stirring at reflux continued for a further 2 h. Thus, the first three steps of the sequence leading to 1,2-dioctyldiselane are conducted in methanol without the isolation of any intermediates. The overall yield of 1-octaneselenol for the 4-step telescoped route, summarized in Scheme 3, (86%) is virtually identical to the 3-step route (Scheme 1) beginning with commercial potassium selenocyanate involving purified intermediates **2a** and **3a**.



Scheme 3. The telescoped process for the synthesis of 1,2-dioctyldiselane.

The synthesis of 1-octaneselenol (**4a**) was performed on a 10.4 mole scale using a 25 L batch reactor equipped with a bleach scrubber. This large-scale process benefited from 4 minor changes to the telescoped route depicted in Scheme 3. Firstly, the suspension of selenium in methanol was cooled to 15 °C before the addition of potassium cyanide (Step 1). The ensuing exothermic reaction raised the internal temperature to 25 °C. Secondly, in Step 3, the potassium carbonate was replaced with potassium hydroxide (1.0 equiv.) with consequent improvement in the ease of stirring. Thirdly, after removal of the volatile impurities from step 3 at 120 °C/0.15 mmHg, the residual 1,2-dioctyldiselane **3a** was used in the next step without distillation. Finally, the reduction of crude **3a** was accomplished with 3.0 equiv. of hypophosphorous acid in refluxing 2-propanol to reduce the reaction time to 9 h giving 1-octaneselenol (**4a**) in an 84% overall yield after distillation.

In order to explore the generality of the telescoped process we synthesized a further eight diselanes **3b-3i** (Scheme 4) on a 23.2–100 mmol scale in 59–94% yield after purification by distillation or crystallization (see Supplementary Information). Reduction of the purified diselanes **3b**–**3i** to the corresponding alkaneselenols **4b-4i** with hypophosphorous acid in refluxing 2-propanol was then accomplished on a 1.8–24.4 mmol scale in 91–98% yield. The data show that the functional groups that are compatible with potassium carbonate in refluxing methanol and hypophosphorous acid (pK_a 1.2) in refluxing 2-propanol include imides, methyl esters, terminal alkenes, sulfones and alcohols.



Scheme 4. The scope of the process for the synthesis of 1-alkaneselenols and 1,2-dialkyldiselanes.

CONCLUSION

In conclusion, we have developed a four-step telescoped process for the synthesis of 1-alkaneselenols that delivers milli- to multi-mole quantities of product with no diminution in the overall yield. Thus, 1-octaneselenol was prepared in an 86% overall yield on a 150 millimole scale and 84% overall yield on a 10.4 mole scale. The first three steps are conducted in one pot in methanol, with the corresponding rate advantage of high concentration (1.0–1.5 M). After removal of the volatile malodorous by-products in Step 3, the residual 1,2-dialkyldiselanes are purified via distillation prior to reduction with hypophosphorous acid in refluxing 2-propanol (Step 4) or they can be reduced directly to the corresponding selenol without distillation. In either case, the yield and purity of the product is the same. The rapid in-situ synthesis of potassium selenocyanate (Step 1) in methanol and its high solubility is especially advantageous.

EXPERIMENTAL

Preparation of potassium selenocyanate (KSeCN). To a magnetically stirred suspension of selenium powder (100 mesh, 7.9 g (100 mmol), 1.0 equiv.) in methanol (100 mL) was added at room temperature potassium cyanide (6.5 g, 100 mmol, 1.0 equiv.) in a single portion. Within a few minutes a mild exothermic reaction ensued raising the internal temperature to 35 °C. As the reaction proceeded, the selenium dissolved leaving a turbid, light grey reaction mixture. After stirring at ambient temperature for 1 h, the reaction mixture was filtered through a 1 cm pad of celite and then concentrated *in-vacuo* to give an off-white solid. The crude potassium selenocyanate was slurried in hot 2-propanol and then allowed to cool to room temperature. The resultant 2-propanol solvate of potassium selenocyanate was collected by filtration and washed with 2-propanol. The labile solvate lost 2-propanol upon storage at 1.0 mm Hg for 16 h at room temperature to give potassium selenocyanate (13.5 g, 93.6 mmol, 94%) as a white solid.

A. Synthesis of 1-octaneselenol with isolation and purification of **2a** and **3a** **(Scheme 1).**

*1. Synthesis of octane-1-selenocyanate (**2a**).* 1-Bromooctane (100 mmol, 1.0 equiv.) was added as a single portion to a magnetically stirred solution of potassium selenocyanate (15.84 g, 110 mmol, 1.1 equiv.) in methanol (75 mL) at room temperature. The reaction mixture was stirred at reflux for 1 h during which time a white precipitate of potassium bromide formed. After cooling to room temperature, the reaction mixture was poured into ice–water (300 mL) and the pale yellow oil extracted into hexanes (2*300 mL). The combined organic extracts (STENCH) were dried (Na_2SO_4) and concentrated *in-vacuo* at ca. 10 °C. The residual yellow oil was purified by short-path distillation. In order to remove the malodorous volatiles, the distillation apparatus was initially fitted with a liquid nitrogen cooled collector and a vacuum (ca 20 mmHg) applied. The pot temperature was increased to ca. 60 °C whereupon a pale yellow distillate (ca 4.0 mL) was collected. After 10 min the vacuum was increased to ca. 1.0 mm Hg in order to remove any remaining volatiles. After fitting a fresh collector, the pot temperature was gradually increased and the octane-1-selenocyanate (**2a**, 20.3 g, 93 mmol, 93%) isolated as a pale yellow oil. bp 97–98 °C/1.0 mm Hg. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.05$ (2H, t, $J = 7.4$, C1H_2), 1.90 (2H, quint, $J = 7.4$, C2H_2), 1.48–1.38 (2H, m, CH_2), 1.38–1.22 (8H, m, 4 ´ CH_2), 0.88 (3H, t, $J = 7.0$, C8H_3). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 101.7$ (SeCN), 31.8 (CH_2), 30.9 (CH_2), 29.8 (C1H_2; $^1J_{Se\text{–}C} = 50.1$), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 22.7 (CH_2), 14.2 (C8H_3). IR (thin film): n = 2150 m (CN) cm^{-1}. See the supporting information for the detection and disposal of cyanide.

*2. Synthesis of 1,2-dioctyldiselane (**3a**).* A mixture of octane-1-selenocyanate (**2a**, 32.7 g, 150 mmol) and K_2CO_3 (20.7 g, 150 mmol, 1.0 equiv.) in MeOH (150 mL) was heated at reflux for 2 h. After cooling to room temperature, the mixture was poured into H_2O (450 mL). The orange oil that separates was extracted into hexanes (2*225 mL). The aqueous phase containing potassium cyanide was saved for waste treatment as described in the supporting information. The combined organic extracts were washed with H_2O (100 mL), dried (Na_2SO_4) and concentrated *in-vacuo*. The residual orange oil was purified by short path distillation to give 1,2-dioctyldiselane (**3a**, 72.75 mmol, 97%) as an orange oil. bp 150–155 °C/0.03 mm Hg; lit.[22] bp 197–205 °C/3 mm Hg. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.91 (4H, app t, J = 7.3, C1H_2), 1.72 (4H, app quint, J = 7.4, C2H_2), 1.42–1.34 (4H, m, 2 ´ CH_2), 1.34–1.22 (16H, m, 8 ´ CH_2), 0.88 (6H, t, J = 6.9 Hz, C8H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.0 (2C, CH_2), 30.8 (2C, CH_2), 30.1 (2C, CH_2), 29.3 (2C, CH_2), 29.3 (2C, CH_2), 24.1 (2C, CH_2; $^1J_{Se\text{–}C}$ = 60.7), 22.8 (2C, CH_2), 14.2 (2C, CH_3)· LRMS (EI$^+$ mode): m/z = 386 [M$^+$, 100%], 272 (95%), 176 (80%). HRMS (EI$^+$ mode): m/z = 386.0989 [M$^+$, 100%]; calculated for $C_{16}H_{34}Se_2$ [M$^+$]: m/z = 386.0991. ^{1}H NMR data (400 MHz) for dioctyldiselane has been reported.[23] See the Supporting Information for the detection and disposal of cyanide.

*3. Synthesis of 1-octaneselenol (***4a***).* A suspension of 1,2-dioctyldiselane (**3a**, 40.4 g, 105 mmol, 1.0 equiv.) in 2-propanol (100 mL) was heated under reflux until dissolution occurred. Hypophosphorous acid (50% w/v aqueous solution; 20.8 g, 17.3 mL, 157.5 mmol, 1.5 equiv.) was added. Heating at reflux was continued for 17 h whereupon the reaction mixture was allowed to cool to room temperature. H_2O (315 mL) and hexanes (315 mL) were added and the layers separated. The aqueous layer was extracted with hexanes (100 mL) and the combined organic layers were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residual oil was purified by short path distillation to give 1-octaneselenol (**4a**, 38.0 g, 197 mmol, 94%) as a colourless oil. bp 81–85 °C/20 mm Hg; lit.[24] bp 117–120 °C/42 mm Hg. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.58 (2H, q, J = 7.1, C1H_2), 1.69 (2H, quint, J = 7.5, C2H_2), 1.40–1.33 (2H, m, CH_2), 1.33–1.22 (8H, m, 4 ´ CH_2), 0.88 (3H, t, J = 7.0, C8H_2), –0.69 (1H, t, J = 6.8, SeH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 34.1 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 22.7 (CH_2), 17.7 (CH_2;

$^1J_{\text{Se–C}} = 47.4$), 14.1 (CH_3). IR (thin film): n = 2321 w (SeH) cm^{-1}. LRMS (EI$^+$ mode): *m/z* = 194 [M$^+$, 100%]. HRMS (EI$^+$ mode): *m/z* = 194.0580 [M$^+$, 100%]; calculated for $C_8H_{18}Se$ [M$^+$]: *m/z* = 194.0574.

B. One-pot telescoped synthesis of 1,2-dioctyldiselane (3a).

A black suspension of selenium (100 mesh, 13.03 g, 165 mmol, 1.1 equiv.) and potassium cyanide (11.72 g, 180 mmol, 1.2 equiv.) in methanol (100 mL) was stirred at ambient temperature for 1 h forming a pale grey turbid reaction mixture containing potassium selenocyanate. 1-Bromooctane (29.0 g, 150 mmol, 1.0 equiv.) was added to the reaction mixture in one portion and the resulting grey suspension heated under reflux for 1 h forming a yellow/brown suspension. Anhydrous potassium carbonate (20.7 g, 150 mmol, 1.0 equiv.) was then added to the reaction mixture in one portion and the resulting yellow suspension heated under reflux for 2 h. The reaction mixture was poured into ice–water (300 mL) and the mixture extracted with hexanes (2*100 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated *in-vacuo* to give the crude title compound that was purified by short-path distillation. A yellow malodorous forerun (*ca*. 3 g) was collected in a liquid nitrogen cooled receiver at a pot temperature of 60 °C (1.0 mm Hg). After changing the receiver, the 1,2-dioctyldiselane **3a** (26.52 g, 69.0 mmol, 92%) distilled at 150–155 °C/0.03 mmHg. KOH (8.4 g, 150 mmol, 1.0 equiv.) dissolved in H_2O (ca. 10 mL) can be added to the crude 1-octaneselenocyanate instead of anhydrous K_2CO_3.

SUPPORTING INFORMATION

General information and materials including cyanide waste management, experimental procedures and characterization data (including ^{1}H and ^{13}C NMR spectra) for 8-tosyloctyl 4-methylbenzenesulfonate (**1h**), 1-octaneselenocyanate (**2a**), 1,2-dialkyldiselanes **3a**–**3i** and 1-alkaneselenols **4a**–**4i** can be found in the supporting information.

AUTHOR INFORMATION

The authors declare no competing financial interest.

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