Rongalite®-promoted odourless and highly regioselective synthesis of β-hydroxyselenides under solvent-free conditions

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An efficient and facile procedure for the odourless and highly regioselective synthesis of β-hydroxyselenides by the ring-opening of epoxides with 1,2-diphenyldiselenide in the presence of Rongalite® and K_2CO_3 under solvent-free conditions on grinding has been developed. The important features of this methodology are high yields, reasonably rapid reaction rate, simple workup, high regioselectivity and no requirement for metal catalysts.

Keywords: Rongalite®, β-hydroxyselenides, grinding, solvent-free conditions

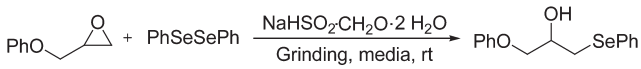
Great advances in organoselenium chemistry have been made during the last few decades. Organoselenium compounds, for example, have shown an important role in organic chemistry, acting as versatile and useful reagents in organic synthesis[1–3] as well as in pharmaceutical synthesis.[4–6] β-Hydroxyselenides are highly valuable intermediates in several organic transformations.[7–11] As a result, a number of synthetic methods to prepare these compounds have been described. Classical synthesis of β-hydroxyselenides involves the ring opening of an epoxide by an excess of benzeneselenol, which inevitably incurs anunpleasant odour, either catalysed by $Ti(O^iPr)_4$,[12] ammonium-12-molybdophosphate (AMP)[13] or under supramolecular catalysis in the presence of β-cyclodextrin in water.[14] Recently, Yang and coworkers reported the synthesis of β-hydroxyselenides using $[bmim]BF_4$ as catalyst.[15] However, ionic liquids, especially imidazolium-based systems containing BF_4 anions, are toxic in nature because they liberate hazardous HF and their high cost and difficult disposal make their utility limited.[16] Thus, the method has been developed for the synthesis of β-hydroxyselenides by the reaction of epoxides with 1,2-diphenyldiselenide using different promoting agents. These promoting agents include Sm-TMSCl,[17] ytterbium(III) chalcogenolate complexes,[18] $NaBH_4$/NaOH under microwave irradiation[19] or traditional heating,[20] tetrathiomolybdate,[21] indium compounds,[22,23] PBu_3,[24] zinc compounds[25,26] and sulfite/base in DMF.[27] Other methods include ring opening of epoxides with tributylstannyl phenylselenolate ($Bu_3SnSePh$) in the presence of $BF_3{\cdot}Et_2O$,[28] phenylselanylzinc(II) chloride (PhSeZnCl),[29] phenylseleno hydroxylation of alkenes with 1,2-diphenyldiselenide and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[30] and thermal reaction of alkyl aryl selenoxides in the supercage of zeolite NaY.[31]

Although the syntheses of β-hydroxyselenides involving some of the above-mentioned methods have their own advantages, each suffers from one or more limitations such as the use of unpleasant smelling substrates[12–15] and expensive, toxic or metallic catalysts,[18] long reaction times,[24] unsatisfactory yields[28] as well as the use of organic solvents,[27] which leaves scope for further development of new environmentally clean syntheses. Therefore, developing versatile approaches to synthesise β-hydroxyselenides selectively still remains a highly desired goal in organic synthesis.

Recently, we reported Rongalite®-promoted ring opening of epoxides with disulfides[32] and thia-Michael addition of disulfides to α,β-unsaturated carbonyl compounds[33] in the presence of base (Rongalite® is sodium formaldehyde sulfoxylate, $NaHSO_2{\cdot}CH_2O{\cdot}2H_2O$ an inexpensive reagent). As a continuation of our research in this area, we expected to apply the Rongalite®/base system in the ring opening of epoxides with 1,2-diphenyldiselenide. Herein, we report a highly practical method to access β-hydroxyselenides by Rongalite® and base-promoted cleavage of 1,2-diphenyldiselenide and a subsequent ring-opening reaction under solvent-free conditions.

The model reaction of 2-(phenoxymethyl)oxirane (**1a**) with 1,2-diphenyldiselenide was conducted to screen for optimal reaction conditions on grinding under solvent-free conditions at room temperature. At the onset of the research, different reaction media such as basic Al_2O_3, silica gel, neutral Al_2O_3 and acidic Al_2O_3 were tested to find the optimal conditions (Table 1, entries 1–4). As shown in Table 1, acidic Al_2O_3 was determined to be the most suitable medium, which afforded the desired product 1-phenoxy-3-(phenylselanyl)propan-2-ol (**2a**) in excellent yield (Table 1, entry 4). It was found that **2a** was not obtained in the absence of a base (Table 1, entry 5). Among the screened bases, Et_3N, Cs_2CO_3, $KF{\cdot}2H_2O$ and K_3PO_4 provided only 24%, 80%, 49% and 66% yield of **2a**, respectively (Table 1, entries 6–9). However, it was satisfying to find that the reaction could reach completion in as little as 5 min and afford **2a** in 96% yield when the combination of K_2CO_3 and acidic Al_2O_3 was employed at room temperature in the presence of 3 equiv. of Rongalite® (Table 1, entry 4). Moreover, the yield was significantly affected by the amount of Rongalite® (Table 1, entries 10–13). The results indicated that the yield was decreased to some extent when 2 equivalents

Table 1 Screening conditions[a]



1a **2a**

Entry	Rongalite®/equiv.	Base (equiv.)	Media	Yield/%[b]
1	3	K_2CO_3 (1.5)	Basic Al_2O_3	66
2	3	K_2CO_3 (1.5)	Silica gel	59
3	3	K_2CO_3 (1.5)	Neutral Al_2O_3	85
4	3	K_2CO_3 (1.5)	Acidic Al_2O_3	96
5	3	–	Acidic Al_2O_3	NR
6	3	Et_3N (1.5)	Acidic Al_2O_3	24
7	3	Cs_2CO_3 (1.5)	Acidic Al_2O_3	80
8	3	$KF{\cdot}2H_2O$ (1.5)	Acidic Al_2O_3	49
9	3	K_3PO_4 (1.5)	Acidic Al_2O_3	66
10	–	K_2CO_3 (1.5)	Acidic Al_2O_3	NR
11	2	K_2CO_3 (1.5)	Acidic Al_2O_3	82
12	1	K_2CO_3 (1.5)	Acidic Al_2O_3	64
13	0.5	K_2CO_3 (1.5)	Acidic Al_2O_3	21
14	3	K_2CO_3 (1)	Acidic Al_2O_3	62

NR = No reaction.
[a]The reaction was run with: 2-(phenoxymethyl)oxirane (0.5 mmol), 1,2-diphenyldiselenide (0.2 mmol), $NaHSO_2{\cdot}CH_2O{\cdot}2H_2O$ (0.6 mmol), K_2CO_3 (0.3 mmol), acidic Al_2O_3 (500 mg) by grinding at room temperature for 5 min under solvent-free conditions.
[b]Isolated yield.

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of Rongalite® were added, and no reaction was observed even for a longer time in the absence of Rongalite® (Table 1, entry 10). Decreasing the amount of K_2CO_3 in the system reduced the yield slightly (Table 1, entry 14).

With the optimal reaction conditions in hand, to extend the scope and generality of this method, a variety of epoxides were subjected to the ring opening reaction with 1,2-diphenyldiselenide to give β-hydroxyselenides in impressive yields and the results are summarised in Table 2.

In the case of alkyl-substituted unsymmetrical epoxides (**1a–e**), the reaction proceeds with a remarkable regioselectivity to give only one β-hydroxyselenide isomer **(2a–e)** of the two possible regio-isomers (**2** and **3**) as a result of the exclusive attack of the selenide anions on the less hindered carbon of the epoxide (Table 2, entries 1–5).

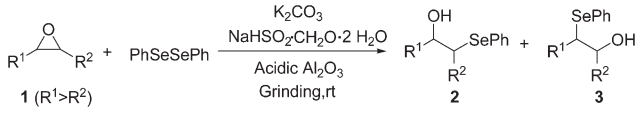
On the other hand, the ring-opening of a symmetrical epoxide, such as cyclohexene oxide (**1f**) with 1,2-diphenyldiselenide gave *trans*-2-(phenylselanyl)cyclohexanol (**2f**) with high stereoselectivity in good yields (Table 2, entry 6). The ^{1}H NMR spectra indicated that only the *trans*-isomer was formed.

Moreover, when epoxides containing a double-bond or an ester group, such as 2-(oct-7-enyl)oxirane (**1g**), 2-(allyloxymethyl)oxirane (**1h**) and oxiran-2-ylmethyl methacrylate (**1i**) were used, the corresponding products of **2g**-**2i** were afforded with yields which ranged from moderate to good (Table 2, entries 7-9). Unfortunately, attempts to ring open **1a** with a dialkyl diselenide, such as 1,2-dibenzyldiselenide and 1,2-dimethyldiselenide failed.

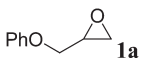
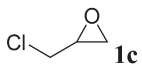
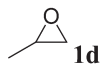
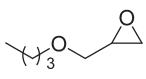
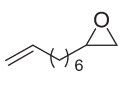
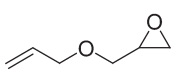
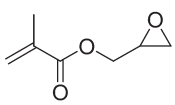
Finally, to expand the scope of the ring-opening reaction, the ring-opening of chiral epoxides [(*S*)-2-(chloromethyl)oxirane (98% ee) or (*R*)-2-(chloromethyl)oxirane (96% ee)] was also examined under the optimised conditions. It was found that optically pure epoxide was converted into the corresponding β-hydroxyselenides *R*-**2c** and *S*-**2c** in good yields without any racemisation or inversion (Scheme 1).

According to the previous proposed mechanism,[34–40] a possible mechanism for the preparation of β-hydroxyselenides has been proposed for the cleavage of 1,2-diphenyldiselenide followed by the ring-opening of epoxides, and the process of the formation of β-hydroxyselenides has been presented in Scheme 2. When treated with a base Rongalite® readily decomposes into HCHO and the HSO_2^- anion (**A**). Intermediate (**A**) then reacts with 1,2-diphenyldiselenide to generate two radical intermediates intermediates (**B** and **D**) and $PhSe^-$ (**C**). The radical (**B**) can also be transformed into the anion (**C**) by reacting with intermediate (**D**). Finally, the nucleophilic attack of the anion (**C**) on the less hindered position of the epoxide affords the desired β-hydroxyselenides.

Table 2 Ring-opening of epoxides with 1,2-diphenyldiselenide in the presence of Rongalite® and K_2CO_3[a]



1 (R^1>R^2) 2 3

Entry	Epoxide	Time /min	Product	Yield/%[b]
1	 **1a**	5	**2a**	96
2	 **1b**	5	**2b**	92
3	 **1c**	15	**2c**	91
4	 **1d**	15	**2d**	85[c]
5	 **1e**	15	**2e**	80
6	 **1f**	15	**2f**	83
7	 **1g**	5	**2g**	92
8	 **1h**	20	**2h**	74[c]
9	 **1i**	5	**2i**	84

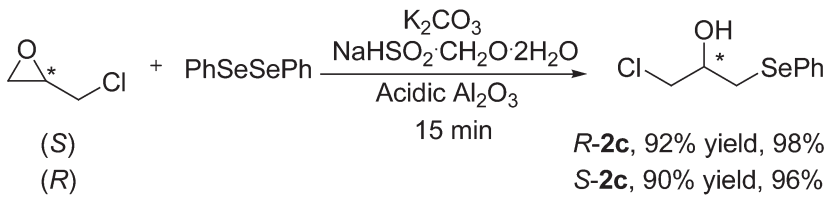
[a]The reaction was run with epoxide (0.5 mmol), 1,2-diphenyldiselenide (0.2 mmol), $NaHSO_2{\bullet}CH_2O{\bullet}2H_2O$ (0.6 mmol), K_2CO_3. (0.3 mmol) and acidic Al_2O_3 (500 mg) at room temperature ground for 5–20min.
[b]Isolated yield of **2**, the regioisomer **3** was not detected.
[c]With epoxide (1 mmol) and $NaHSO_2{\cdot}CH_2O{\cdot}2H_2O$ (1 mmol).

Conclusion

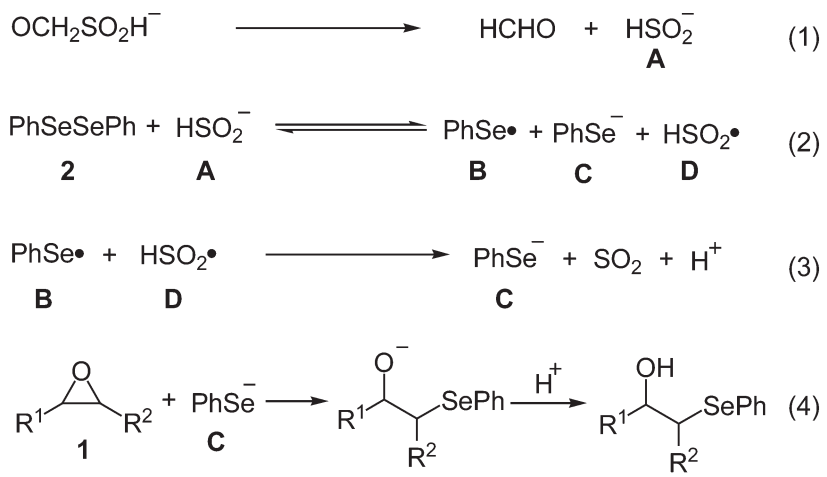
In conclusion, an efficient and simple method for the odourless synthesis of β-hydroxyselenides with high regioselectivity by ring opeing of epoxides with 1,2-diphenyldiselenide by grinding under solvent-free conditions has been developed. Compared with the previously reported methods, the present method has many advantages such as high regioselectivity, high yields, short reaction time, simple operations and no requirement of metal catalysts.

Experimental

Chemicals and solvents were either purchased or purified by standard techniques. IR spectra were recorded on an AVATAR 370 FI-Infrared Spectrophotometer. NMR spectroscopy was performed on both a Bruker-300 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) or 125 MHz (^{13}C NMR). TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC–MS analysis (SHIMADZU GCMS-QP2010). Elemental analyses were carried out using a Carlo-Erba EA1112 instrument. Optical rotations were



Scheme 1 The ring-opening of chiral epoxides with 1,2-diphenyldiselenide



Scheme 2 A possible mechanism for the formation of β-hydroxyselenides.

measured in chloroform on a PolAAr 3005 automatic polarimeter. Enantiomeric excesses (ee) were determined with a HPLC apparatus fitted with a Chiralcel OJ-H (Daicel, Germany) chiral column. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

General procedure

The following components were added to a glass mortar: acidic Al_2O_3 (500 mg), epoxide **1** (batch addition, 0.5 mmol), 1,2-diphenyldiselenide (0.2 mmol), Rongalite® (1 mmol), and K_2CO_3 (0.3 mmol). The mixture was then ground at room temperature for 5-20 min with a glass pestle in the glass mortar. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was washed with ethyl acetate. The combined washings were concentrated under reduced pressure. The pure product was obtained by silica gel column chromatography. The physical and spectroscopic data of compounds **2a**–**k** are as follows.

1-Phenoxy-3-(phenylselanyl)propan-2-ol (**2a**):[19] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.02 (s, 1H), 3.10 (dd, *J* = 12.9 and 5.7 Hz, 1H), 3.18 (dd, *J* = 12.9 and 6.9 Hz, 1H), 3.96–4.01 (m, 2H), 4.08–4.11 (m, 1H), 6.82–6.93 (m, 3H), 7.20–7.26 (m, 5H), 7.49–7.53 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.6, 68.9, 70.3, 114.4, 121.0, 127.1, 129.1, 129.2, 129.3, 132.6, 158.1.

1-(Phenylselanyl)octan-2-ol (**2b**):[23] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, *J* = 10.8 Hz, 3H), 1.17 (s, 7H), 1.32–1.45 (m, 3H), 2.39 (s, 1H), 2.80 (dd, *J* = 12.7 and 8.5 Hz, 1H), 3.05 (dd, *J* = 12.7 and 3.6 Hz, 1H), 3.56–3.59 (m, 1H), 7.15–7.18 (m, 3H), 7.42–7.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.7, 29.2, 31.7, 36.6, 37.2, 69.9, 127.2, 129.1, 129.5, 132.9.

1-Chloro-3-(phenylselanyl)propan-2-ol (**2c**):[23] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.99–3.14 (m, 3H), 3.62–3.64 (m, 2H), 3.92 (s, 1H), 7.20–7.26 (m, 3H), 7.44–7.53 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.3, 48.4, 70.3, 127.6,129.3, 129.4, 133.0.

(R)-1-Chloro-3-(phenylselanyl)propan-2-ol (*R*-**2c**):[23] $[\alpha]_D^{25}$ –21.1 (c 2.52, $CHCl_3$). HPLC analysis using a Chiracel OJ-H column [^{i}PrOH/hexane: 1/99; flow rate: 0.8 mL min^{-1}; detector: 254 nm] showed it to 98% ee. Retention time: t_R(R) 15.45 min, t_R(S) 16.67 min.

(S)-1-Chloro-3-(phenylselanyl)propan-2-ol (*S*-**2c**):[41] $[\alpha]_D^{25}$ +21.7 (c 1.27, $CHCl_3$). HPLC analysis using a Chiracel OJ-H column [^{i}PrOH/hexane: 1/99; flow rate: 0.8 mL min^{-1}; detector: 254 nm] showed it to 96% ee. Retention time: t_S(R) 15.25 min, t_S(S) 16.52 min.

1-(Phenylselanyl)propan-2-ol (**2d**):[23] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17–1.35 (m, 3H), 2.60 (s, 1H), 2.80 (dd, *J* = 12.6 and 4.6 Hz, 1H), 2.99 (dd, *J* = 12.7 and 8.4 Hz, 1H), 3.75–3.81 (m, 1H), 7.15–7.17 (m, 3H), 7.42–7.45 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.7, 38.5, 66.1, 127.3, 129.2, 129.3, 133.1.

1-Butoxy-3-(phenylselanyl)propan-2-ol (**2e**):[12] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3H), 1.25–1.38 (m, 2H), 1.48–1.55 (m, 2H), 2.86 (s, 1H), 3.03–3.07 (m, 2H), 3.37–3.52 (m, 4H), 3.90 (s, 1H), 7.23–7.25 (m, 3H), 7.50–7.54 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 19.2, 29.6,31.5, 31.7, 69.3, 71.2, 73.3, 127.0, 129.0, 129.7, 132.6.

trans-2-(Phenylselanyl)cyclohexanol (**2f**):[23] ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.23–1.42 (m, 4H), 1.1.59–1.73 (m, 2H), 2.11–2.19 (m, 2H), 2.87–2.94 (m, 1H), 3.05 (s, 1H), 3.25–3.38 (m, 1H), 7.24–7.31 (m, 3H), 7.57–7.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.3, 26.7, 33.2, 33.8, 53.3, 72.2, 126.7, 127.9, 128.8, 135.9.

1-(Phenylselanyl)dec-9-en-2-ol (**2g**):[23] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28–1.42 (m, 8H), 1.48–1.52 (m, 2H), 1.98–2.05 (m, 2H), 2.60 (s, 1H), 2.87 (dd, *J* = 12.7 and 4.3 Hz, 1H), 3.10 (dd, *J* = 12.7 and 8.9 Hz, 1H), 3.66–3.67 (m, 1H), 4.90–5.01 (m, 2H), 5.74–5.83 (m, 1H), 7.22–7.25 (m, 3H), 7.49–7.52 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.6, 28.7, 28.8, 29.3, 33.6, 36.5, 37.0, 69.9, 114.1, 127.0, 129.0, 129.5, 132.8, 138.9.

1-(Allyloxy)-3-(phenylselanyl)propan-2-ol (**2h**):[27] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.74 (s, 1H), 3.03–3.09 (m, 2H), 3.46–3.54 (m, 2H), 3.92–3.98 (m, 3H), 5.16–5.28 (m, 2H), 5.82–5.88 (m, 1H), 7.24–7.28 (m, 3H), 7.51–7.55 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 31.8, 69.3, 72.2, 72.7, 117.3, 127.1, 129.1, 129.5, 132.7, 134.2.

2-Hydroxy-3-(phenylselanyl)propyl methacrylate (**2i**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 3H), 2.92 (dd, *J* = 12.9 Hz and 7.5 Hz, 1H), 3.02 (dd, *J* = 12.9 Hz and 5.1 Hz, 1H), 3.89–3.95 (m, 1H), 4.09–4.20 (m, 2H), 5.49 (s, 1H), 6.02 (s, 1H), 7.16–7.44 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 32.0, 67.0, 68.5, 126.0, 127.2, 129.0, 129.1, 132.8, 135.6, 167.1. IR (cm^{-1}): 2984, 1737, 1373, 1234, 1098, 1044. MS (EI, 70 eV) *m/z* (%): 300 (M^+, 12), 69 (100). Anal. Calcd for $C_{13}H_{16}O_3Se$: C, 52.18; H, 5.39; Found: C, 52.22; H, 5.35%.

Electronic Supplementary Information

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