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Discovery, Characterisation, and Utilisation of Selenoxide-Sulfonic acid Salts: A new class of Selenoxide-Based Oxidant and Stable Selenoxide Equivalent.

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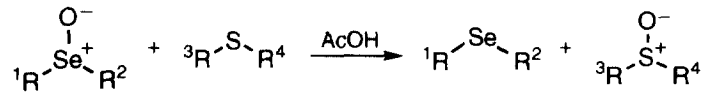
Abstract: The preparation and characterisation of a novel class of salts of selenoxides with sulfonic acids are described. They are readily prepared by simple addition of the sulfonic acid to a solution of selenoxide, and removal of solvent. In most cases they are colourless crystalline solids and are considerably more stable than the parent selenoxides, allowing full characterisation and X-ray crystallographic analysis. They also efficiently oxidise sulfides to sulfoxides, with no overoxidation, and clean regeneration of selenide. Their structure has been confirmed by ^{1}H NMR spectroscopy and X-ray crystallography.

Introduction.

The enantioselective synthesis of sulfoxides is an area of much current research. Early methods, particularly that developed by Andersen[1] and more recently, others[2] involved the use of resolved sulfinate esters and their subsequent reaction with organometallic reagents. A potentially more versatile method of preparation is the enantioselective oxidation of prochiral sulfides. In particular, the reagent systems developed by Kagan,[3] Modena,[4] Davis[5] and Uemura[6] are amongst the most successful at present.[7] Our recent studies on asymmetric sulfur oxidation[8] allowed a comparison between the relative efficiencies of two of the best procedures currently available, namely the modified Sharpless asymmetric oxidation reported by Kagan,[3] and the use of (-) α,α-dichlorocamphorsulphonyloxaziridine developed by Davis.[5] Whilst these procedures worked well in some cases, they both lacked generality (although they are in some cases complementary), and for our systems, significant practical problems were encountered when using them, such as the need for stoichiometric amounts of reagent in the case of the Davis oxaziridine, and removal of titanium and tartrate residues from the crude product in the Modena and Kagan systems. Although alternative procedures were available, we decided to initiate a programme to develop our own asymmetric oxidising agents, which we hoped would be a significant advance on current methodology, and could be extended to oxidise other substrates as well as sulfides.

We chose to study and further develop a reaction first published in 1959, which employed the use of selenoxides for the oxidation of dialkyl sulfides to sulfoxides (scheme 1).[9,10] We found this reaction to be particularly interesting for a number of reasons. Firstly, the mechanism of the reaction was of interest, and may be of relevance to our related work on thiosulfonium salts.[11] The reaction also has widespread potential applicability, as its is known that selenoxides will oxidise a wide variety of substrates, including sulfides and thiols, tertiary amines,[12] phosphines,[10] catechols and hydroquinones.[13] We believe there is also potential for a catalytic asymmetric process which is our long-term goal.



$R^1 = R^2 = PhCH_2$, *p*-(MeO)C_6H_4; $R^3 = R^4$ = alkyl

Scheme 1

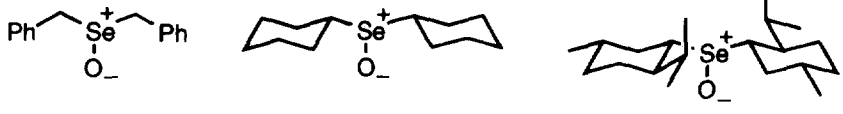
Organoselenium compounds have been used extensively in organic synthesis.[14] Selenoxides have been exploited primarily as precursors to α,β-unsaturated carbonyl compounds,[15] and more recently, there have been an increasing number of reports of their use in asymmetric synthesis, for example in the preparation of enantiomerically enriched allylic alcohols *via* 2,3-sigmatropic rearrangements of allylic selenoxides,[16] or allenes and alkenes by elimination of selenenic acid,[17,18] *via* enantiomerically enriched selenoxides produced either by asymmetric oxidation or chirality transfer. Chiral diselenides have also recently been reported as enantioselective selenylating agents.[19] However, to the best of our knowledge, no successful selenium-based asymmetric oxidising agents have so far been reported.

Discovery.

Since the original reports[9,10,14] of selenoxide based oxidations, relatively little work has followed. This is at least partly a result of the presumed instability of such species. Indeed, selenoxides are well known for their propensity for β-elimination reactions, a procedure which has been extensively exploited for the synthesis of unsaturated carbonyl compounds, as mentioned above.[15] Dialkyl selenoxides are much less prone to such a reaction,[20] and many are isolable. However, an alternative mode of degradation for these compounds exists in which they can revert to the parent selenides over a period of hours. For example, dimenthyl selenoxide (3) reverts cleanly back to the selenide after approximately 12 hours at room temperature.

Early work on the oxidation of sulfides to sulfoxides using benzylselenoxide[9] and (4-methoxyphenyl)selenoxide[10] involved the use of acetic acid as solvent (scheme 1). Our initial interest lay in developing a novel selenoxide oxidation system, initially for the oxidation of sulfides, that would operate under mild conditions, in a more practically useful solvent such as dichloromethane. This would then provide the basis for the development of an asymmetric sulfur oxidation procedure.

We initially began by synthesising a number of representative selenoxides, *viz.* benzyl selenoxide (1), prepared according to the literature procedure,[9] and cyclohexyl- (2) and menthyl (3) selenoxides, prepared from the Grignard reagents derived from cyclohexyl bromide and menthyl chloride respectively, and quenching with $SeOCl_2$ (<0.5 eq.).[21] Note that intermediate symmetrical selenoxides produced in the Grignard reaction revert to the corresponding selenides under the reaction conditions, but can be reoxidised efficiently using MCPBA.



1 **2** **3**

We then began to investigate the oxidation reaction. With simple mixtures of selenoxides and sulfides in organic solvents such as dichloromethane, no reaction occurred.[22] It thus became apparent that the acetic acid was playing a role in the original literature procedure. In an attempt to mimic this, one equivalent of *p*-toluene

sulfonic acid was added to a solution of benzylselenoxide and methylsulfide in CH_2Cl_2, however oxidation still took place only very slowly. By following the oxidations by ^1H NMR, it became clear that signals due to the original selenoxide had been replaced by other signals where the protons adjacent to the selenium atom were considerably more deshielded. This effect was found to be due to interaction of the selenoxide with the sulfonic acid, and was further investigated in the absence of the sulfide substrate. Thus addition of a variety of anhydrous sulfonic acids, including *p*-toluene-, *p*-bromobenzene-, trifluoromethyl- and 2,2,2-trifluoroethyl sulfonic acids, to our three initial selenoxides in dichloromethane, all showed an analogous deshielding. It should be noted that this effect was not observed with acetic acid. Removal of solvent, in most cases[23] leaves a colourless solid which can be recrystallised and fully characterised, a procedure which was not possible with the corresponding selenoxides. Selected physical data are shown in table 1.[24]

Table 1. Selected Physical Data for Selenoxide Sulfonic Acid Salts.

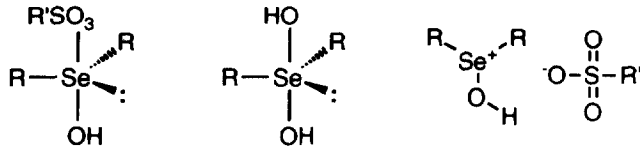
Entry	Selenoxide	Sulfonic acid	^1H NMR[a]	M.P. (°C)
1	3	*p*-Toluene	3.85, 3.40	b
2	3	*p*-Bromobenzene	3.74, 3.35	b
3	3	2,2,2-Trifluoroethane	3.84, 3.49	46.2-50.2
4	2	*p*-Toluene	3.71	108.1-110.0
5	2	*p*-Bromobenzene	3.68	96.1-98.4
6	2	2,2,2-Trifluoroethane	3.89	80.6-83.3
7	1	*p*-Toluene	4.66, 4.14	107.5-108.0
8	1	*p*-Bromobenzene	4.63, 4.15	121.7-122.7
9	1	Trifluoromethane	4.57, 4.12	c
10	1	2,2,2-Trifluoroethane	4.61, 4.11	94.4 - 96.5

Notes: [a] δ, $CDCl_3$, 25°C, resonances given are chemical shifts of protons α to selenoxide, see experimental section for further details. Corresponding values for parent selenoxides are **1**, 2.93, 2.86, **2**, 2.88, **3**, 3.94, 3.99; [b] oil at room temperature; [c] see reference 23.

Characterisation.

There were a number of possible alternatives for the structure of the adducts formed between the selenoxides and sulfonic acids. Importantly, the ^1H NMR spectra of the part of the adduct originally derived from the selenoxide, showed little variation between sulfonic acids (table 1, *cf.* entries 7 and 9). This, we believe, rules out the possibility of these adducts being any kind of selenurane[25] intermediate (4) although the possibility of a small equilibrium concentration cannot be discounted. If such a selenurane were present then considerable variation of chemical shift of the protons α-to selenium would be expected, depending on the

sulfonic acid used. The reactions were also performed under rigorously anhydrous conditions, so formation of the hydrate (5) was also ruled out.[16-18]



4 **5** **6**

We believe a much more likely candidate, at least in solution, is the hydroxy selenonium salt structure (6). The isolation and full characterisation of such an intermolecular complex is, to the best of our knowledge, the first of its kind, although compounds containing intramolecular hydrogen bonds between selenoxides and either hydroxyl or amide groups have been proposed.[26] Complexes between a selenoxide and some inorganic acids,[27] and 2,2'-dihydroxy-1,1'-binaphthol[28] have also been reported. Although relatively little is known about the basicity of selenoxides, they would be expected to be more basic than sulfoxides, because of the greater difference in electronegativities between the selenium and oxygen atoms. Sulfoxides are known to be of similar basicity to amide oxygen atoms[29] and so the formation of salt-like structures is not unreasonable.

One important aspect of these salts is that they are considerably more stable than the parent selenoxides, and so are potentially very useful for selenoxide characterisation. There have been remarkably few X-ray crystal structures of selenoxides reported in the literature, and those that have, have been specifically designed for enhanced stability.[30] The stability of our salts has allowed us to obtain an X-ray crystal structure of the complex between *p*-bromobenzenesulfonic acid and cyclohexyl selenoxide (7) (figure 1).[31] This clearly shows the structure, at least in the solid state, to be that of the salt-like species suggested by the earlier NMR evidence. The protonated selenoxide oxygen can be clearly seen, as can the hydrogen bond from this proton to the oxygen atom of the sulfonate group. The O-H bond length in the salt is 0.83Å (*cf.* 0.96Å for the O-H in methanol) and the hydrogen bond length is 1.78Å (*cf.* 1.79Å in ice[32]). The bond angle O^1-H-O^2 is 169°, which is consistent with the presence of a hydrogen bond. Analysis of X-ray crystallographic data has shown that most hydrogen bonds are non-linear by approximately 10-15°.[33]

Utilisation.[22]

Whilst the formation of these novel salts was of great interest in itself, we were particularly interested in whether they were capable of carrying out the desired oxidation reaction. As mentioned earlier, when benzyl selenoxide was mixed with *p*-toluene sulfonic acid and methyl sulfide, oxidation of the sulfide was observed, but the reaction was only very slow taking around a week to reach completion, which was clearly unsatisfactory. The use of *p*-bromobenzene sulfonic acid also gave a slow reaction. It was found that the much stronger trifluoromethanesulfonic acid, at low temperature, activated the oxidation to a far greater extent, a typical reaction going to completion in 24h at -30°C using menthylselenoxide (table 2). However, when used with benzyl selenoxide (1), decomposition by nucleophilic attack of sulfide α to selenium was seen to be the major reaction with only a low yield of sulfoxide being isolated (scheme 2). Fortunately, by using 2,2,2-trifluoroethane sulfonic acid in conjunction with menthylselenoxide, the oxidation proceeded at room temperature in a rapid, clean and efficient manner (table 2). Other sulfonic acids, such as camphor-10-sulfonic acid can also be used efficiently in this reaction (table 2, entry 13) although no asymmetric induction is observed. Importantly, in all cases except that mentioned above, the regenerated selenide can be easily recovered in high yield.

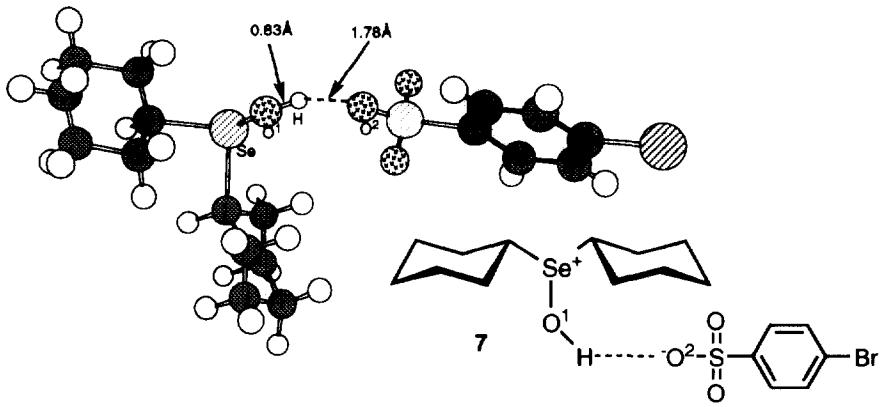
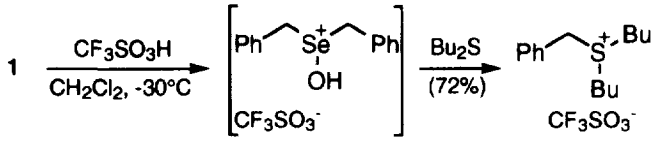


Figure 1: X-ray Crystal Structure of salt between **2** and *p*-bromobenzene sulfonic acid.

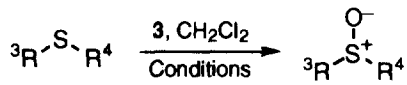


Scheme 2

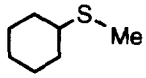
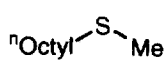
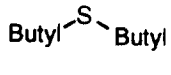
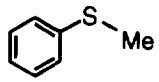
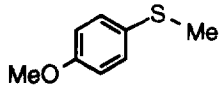
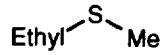
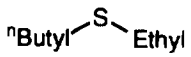
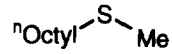
Variation of the selenoxide also proved very important to the efficiency of the oxidation reaction. Surprisingly, cyclohexylselenoxide (2) gave poor yields of sulfoxide in general, whilst benzylselenoxide (1), led to decomposition products if used in conjunction with trifluoromethane sulfonic acid, as previously mentioned. The oxidation of various sulfides was carried out using menthylselenoxide (1) with trifluoromethane- (system A), 2,2,2- trifluoroethane- (system B) and (1R)-(-)-camphor-10-sulfonic acids (system C). As can be seen from the table, good to excellent yields of sulfoxide were obtained for dialkyl sulfides, particularly using systems B and C, however, arylalkyl sulfides proved to be far less reactive. Introduction of an electron-releasing methoxyl group at the *para* position in methyl phenyl sulfide increased the reactivity of the sulfide to oxidation markedly, however the reaction was still poor compared with that for dialkyl sulfides.

Menthylselenoxide (3) is, to the best of our knowledge, the first homochiral selenoxide-based oxidising agent. As such it was envisaged that this compound could induce asymmetry in the oxidation process resulting in the generation of an optically active sulfoxide. Oxidations of prochiral dialkyl sulfides with menthylselenoxide (3) and trifluoromethane-, 2,2,2-trifluoroethane- and (1R)-(-)-camphor-10-sulfonic acids, have so far resulted in sulfoxides of low (<10%) enantiomeric excess. We are currently developing new synthetic routes to superior homochiral selenoxides, and carrying out mechanistic studies which we believe will help in the rational design of new asymmetric selenoxide based oxidants.

Table 2: Oxidation of Sulfides to Sulfoxides using Menthyl Selenoxide-Sulfonic acid salts.



Conditions: **A**, CF_3SO_3H, -25°C; **B**, $CF_3CH_2SO_3H$, RT; **C**, (1R)-(-)-Camphor-10-sulfonic acid, -30°C.

Entry	Sulfide	Conditions	Time	Yield (%)
1		**A**	20h	60
2		**B**	2h	94
3		**A**	24h	78
4		**B**	30min	90
5		**A**	42h	66
6		**B**	45min	86
7		**A**	144h	5
8		**A**	60h	30
9		**B**	120h	30
10		**A**	20h	48
11		**B**	2h	92
12		**B**	1h	87
13		**C**	1h	88

Summary.

We believe that the isolation and characterisation of new, stable selenoxide salts will greatly facilitate the use of selenoxides in synthesis, and we are currently investigating their properties further. These salts are mild and efficient oxidising agents for dialkylsulfides, and oxidations proceed with clean regeneration of the selenide in solvents such as CH_2Cl_2 when used either preformed, or generated *in situ*. Fine-tuning of both the selenoxide and sulfonic acid is possible to optimise conditions for efficient oxidation. We are currently working on the development of an asymmetric sulfur oxidation procedure utilising this system, and are also looking at its application to the oxidation of other substrates.

Acknowledgements. We thank the former Science and Engineering Research Council for an earmarked studentship (DJP), and ICI Strategic Research Fund and the Royal Society for additional financial support.

Experimental Section.

Melting points were recorded on a Reichert Hot Stage apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded for ^{1}H at 300 MHz, ^{13}C at 75 MHz, on a General Electric QE 300 machine, for ^{1}H at 400 MHz, ^{13}C at 100.6 MHz, on a Bruker AM 400 spectrometer, or for ^{1}H at 250.6 MHz, ^{13}C at 62.9 MHz, on a Bruker ARX 250 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield of tetramethylsilane (singlet at 0 ppm, TMS) for proton resonance and referenced to the central peak of the triplet for deuterated chloroform (77.0 ppm) for ^{13}C resonances.

Infrared spectra were recorded on a Phillips PU 8706 infrared spectrophotometer and signals were referenced to a peak at 1601cm^{-1} for polystyrene. Mass spectra were recorded on a VG Autospec mass spectrometer. Optical rotations were measured on an Optical Activity AA-1000 polarimeter. Microanalyses were carried out at the University of Leeds Microanalytical Laboratory. All C, H, N and S analytical figures are percentage figures.

Thin layer chromatography was carried out using precoated aluminium (or plastic) backed silica plates which were visualised using ultraviolet light, permanganate, or anisaldehyde stain. Column chromatography was carried out on Merck silica (230-400 mesh) unless otherwise stated.

All solvents were dried and distilled before use by usual procedures.[34] Similar purification for other reagents was also carried out prior to use. Pet. ether refers to petroleum ether (b.p. 40-60 °C) unless otherwise stated.

Benzyl selenide[35]

To a suspension of selenium (2.30g, 29.0mmol, 1eq) in H_2O (25ml) was added sodium borohydride (2.30g, 61.0mmol, 2eq) and the solution stirred at room temperature for 10min. Benzyl chloride (7.30g, 58.0mmol, 2eq) was then added gradually to the stirred solution and the reaction left for 18h at room temperature. The precipitate was then collected by filtration and washed with H_2O (20ml). Recrystallisation gave benzyl selenide (2.27g, 8.70mmol, 30%) as colourless needles, mp 43.8-45.0°C (hexane); δ_H (300 MHz; $CDCl_3$) 3.72 (4H, s, CH_2Se) and 7.24-7.29 (10H, m, ArH); δ_C (100 MHz; $CDCl_3$) 27.60 (CH_2Se-1), 126.66 (ArCH), 128.44 (ArCH), 128.94 (ArCH) and 139.15 (ArC-2); ν_{max} (CH_2Cl_2)/cm^{-1} 3000-2900m (C-H), 1585m (C=C), 1480m (C=C), 1440 (-CH_2-), 1325m, 1200s, 1170m, 1140m and 1050s; MS (EI) *m/z* 261 (M^++1, 29%), 181(6), 91(100), 65(23) and 39(9); (Found: C, 64.40; H, 5.30. Calc. for $C_{14}H_{14}Se$: C, 64.37; H, 5.40%).

Benzyl selenoxide 1[35]

To a solution of benzyl selenide (43.0mg, 0.16mmol, 1eq) in CH_2Cl_2 (2ml) was added saturated K_2CO_3 (0.20ml). *m*CPBA (55%, 52.0mg, 0.16mmol, 1eq) in CH_2Cl_2 (2ml) was then added dropwise and the reaction left stirring for 1h. H_2O (4ml) was then added and the aqueous layer separated and extracted with CH_2Cl_2 (2x4ml). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo* to give crude selenoxide (34.4mg, 0.12mmol, 80%) as a white solid. Recrystallisation gave **1** as colourless needles, mp 110.0-112.3°C ($CHCl_3$/hexane); δ_H (300 MHz; $CDCl_3$) 3.94 (2H, d, J 12.0 Hz, CH_2Se), 3.99 (2H, d, J 12.0 Hz, CH_2Se), 7.25-7.35 (4H, m, ArH) and 7.37-7.40 (6H, m, ArH); δ_C (75 MHz; $CDCl_3$) 53.19 (CH_2Se-1), 128.31 (ArCH), 129.08 (ArCH), 129.64 (ArCH) and 130.66 (ArC-2); ν_{max} (Nujol)/cm^{-1} 3000-2900s (C-H), 1590m (C=C), 1490s (C=C), 1440m (-CH_2-), 1350s, 1170s, 1050s and 800s (Se=O); MS (EI) *m/z* 277 (M^+,

2%), 262(M-O, 14), 139(17), 91(100), 77(8), 65(23) and 51(7) (Found: C, 60.75; H, 5.05. Calc. for $C_{14}H_{14}OSe$: C, 60.66; H, 5.09%).

Benzyl selenoxide / *p*-toluenesulfonic acid salt

To a solution of benzyl selenoxide **1** (51.0mg, 0.18mmol, 1eq) in CH_2Cl_2 (4ml) was added *p*-toluene sulfonic acid (32.0mg, 0.18mmol, 1eq) and the solution stirred at room temperature for 30min. Concentration *in vacuo* gave the crude salt as a colourless solid. Recrystallisation gave the benzyl selenoxide / *p*-toluene sulfonic acid salt as colourless needles (58.0mg, 0.17mmol, 90%), mp 107.5-108.0°C (ethanol/water); δ_H (300 MHz; $CDCl_3$) 2.42 (3H, s, $ArCH_3$), 4.14 (2H, d, J 12.0 Hz, CH_2Se), 4.66 (2H, d, J 12.0 Hz, CH_2Se), 7.24-7.31 (12H, m, ArH) and 7.76 (2H, d, J 7.8 Hz, ArH); δ_C (100 MHz; $CDCl_3$) 21.40 (CH_3), 51.94 (CH_2Se-1), 125.87 (ArCH), 128.35 (ArC), 128.80 (ArCH), 129.04 (ArCH), 129.29 (ArCH), 131.23 (ArCH), 140.78 (ArC) and 141.50 (ArC); ν_{max} (CH_2Cl_2)/cm^{-1} 3000-2900s (C-H), 1600w (C=C), 1500w (C=C), 1420m (SO_2-O), 1200s (SO_2-O), 1150s, 1100s, 1020s and 990s (Se=O); MS (EI), inconclusive; (Found: C, 56.05; H, 4.85; S, 7.35. $C_{21}H_{22}O_4SSe$ requires C, 56.12; H, 4.93; S, 7.14%).

Benzyl selenoxide / *p*-bromobenzenesulfonic acid salt

To a solution of benzyl selenoxide **1** (200mg, 0.72mmol, 1eq) in CH_2Cl_2 (4ml) was added anhydrous *p*-bromobenzene sulfonic acid (171mg, 0.720mmol, 1eq) and the solution stirred for 30min at room temperature. Concentration *in vacuo* gave the crude salt which was recrystallised to give the benzyl selenoxide / *p*-bromo benzene sulfonic acid salt (333mg, 0.65mmol, 90%) as colourless needles, mp 121.7-122.7°C (ethyl acetate); δ_H (400 MHz; $CDCl_3$) 4.15 (2H, d, J 12.0 Hz, CH_2Se), 4.63 (2H, d, J 12.0 Hz, CH_2Se), 7.26-7.36 (10H, m, ArH), 7.58 (2H,d, J 8.52 Hz, ArH) and 7.70 (2H, d, J 8.5 Hz, ArH); δ_C (100 MHz; $CDCl_3$) 52.14 (CH_2-1), 125.04 (ArC), 127.66 (ArCH), 128.13 (ArC), 128.94 (ArCH), 129.50 (ArCH), 131.14 (ArCH), 131.63 (ArCH) and 143.07 (ArC); ν_{max} (thin film)/cm^{-1} 3000-2900m (C-H), 1600w (C=C), 1450m (C=C), 1420m (SO_2-O), 1200s (SO_2-O) and 990s (Se=O); MS (EI), inconclusive; (Found: C, 46.65, H, 3.60; S, 6.34. $BrC_{20}H_{19}O_4SSe$ requires C, 46.71; H, 3.72; S, 6.24%).

Benzyl selenoxide / 2,2,2-trifluoroethane sulfonic acid salt

To a solution of benzyl selenoxide **1** (200mg, 0.72mmol, 1eq) in CH_2Cl_2 (5ml) was added 2,2,2-trifluoroethane sulfonic acid (0.09ml, 0.72mmol, 1eq) and the solution stirred at room temperature for 20min. Concentration *in vacuo* gave the crude salt as a white solid (302mg, 0.66mmol, 95%). Recrystallisation gave the benzyl selenoxide / 2,2,2-trifluoroethane sulfonic acid salt as colourless needles, mp 94.4 - 96.5°C (ethyl acetate); δ_H (400 MHz; $CDCl_3$) 3.63 (2H, q, $^3J(^1H\text{-}^{19}F)$ 9.6 Hz, CH_2CF_3), 4.11 (2H, d, J 12.0 Hz, CH_2Se), 4.61 (2H, d, J 12.0 Hz, CH_2Se) and 7.31-7.40 (10H, m, ArH); δ_C (100 MHz; $CDCl_3$) 52.09 (CH_2Se, $^1J(^{13}C\text{-}^{77}Se)$ 144.0 Hz), 53.61 (CH_2CF_3, q, $^2J(^{13}C\text{-}^{19}F)$ 119.8 Hz), 122.80 (CF_3, q, $^1J(^{13}C\text{-}^{19}F)$ 1098.3 Hz), 128.02 (ArC), 128.98 (ArCH), 129.60 (ArCH) and 131.23 (ArCH); ν_{max} (CH_2Cl_2)/cm^{-1} 3000m (C-H), 1500m, 1450m (C=C), 1400m (SO_2-O), 1350s, 1200s (SO_2-O), 1150s, 1080s and 1020s (Se=O); MS (EI), inconclusive; (Found: C, 43.35; H, 3.65; S, 7.40. $C_{16}F_3H_{17}O_4SSe$ requires C, 43.55; H, 3.88; S, 7.27%).

L-Menthyl chloride[21d]

To a solution of anhydrous zinc chloride (250g, 1.83mol, 3.5eq) in HCl (37% aqueous solution, 170ml) at 0°C was added L-menthol (83.0g, 0.53mol, 1eq). The mixture was stirred at 60°C for 12h, cooled and then extracted with petroleum ether (4x200ml). The organic extracts were then repeatedly washed with conc. H_2SO_4 (5x30ml) until the washing no longer gave an orange colour, dried ($MgSO_4$) and concentrated *in vacuo*.

Distillation (bp 100-101°C/25mmHg) gave L-menthyl chloride as a colourless oil (84.7g, 0.48mol, 91%); δ_H (300 MHz; $CDCl_3$) 0.78 (3H, d, J 7.1, CH*Me*), 0.95 (6H, d, J 7.0, CH(*Me*)$_2$), 1.30-1.49 (4H, m), 1.55-1.59 (1H, m), 1.68-1.77 (2H, m), 2.22-2.30 (1H, m), 2.31-2.40 (1H, m) and 3.80 (1H, dt, J 7.8, 4.1 Hz, CHCl); $[\alpha]_D^{20}$ -52.4° (neat) ($[\alpha]_D^{20}$ -53.0 (neat)[21d]).

Menthyl selenide

To a suspension of magnesium turnings (8.10g, 0.33mol, 1.1eq) in anhydrous diethyl ether (10ml) was added several crystals of iodine. L-Menthyl chloride (*freshly distilled*, 2ml) was added and an exothermic reaction was seen to oocur. The remaining menthyl chloride (56.0ml, 0.300mol, 1eq) in diethyl ether (50ml) was then added dropwise at a rate sufficient to maintain gentle reflux. After addition was complete, the solution was heated under reflux for 1h then allowed to cool. Selenium oxychloride (20.0g, 0.12mol, 0.4eq) in diethyl ether (50ml) was then added cautiously and the resulting solution heated under reflux for a further 1h. H_2O (50ml) was cautiously added and the aqueous layer then separated and extracted with diethyl ether (3x50ml). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo*. An aliquot of the crude product mixture (6.90g) was purified by column chromatography [silica gel, petroleum ether (bp 40-60°C) as eluant] giving menthyl selenide (2.35g, 6.57mmol, 32% based on $SeOCl_2$). Recrystallisation gave colourless needles, mp 73.8-76.3°C (methanol); δ_H (300 MHz; $CDCl_3$) 0.77 (6H, d, J 6.9 Hz, *Me*CH), 0.83-1.12 (16H, m), 1.20-1.40 (6H, m, CH_2CH_2), 1.72 (4H, t, J 11.4 Hz), 2.11 (2H, d, J 10.5 Hz), 2.27 (2H, dt, J 6.9, 2.4 Hz) and 2.81 (2H, dt, J 11.4, 3.6 Hz, CHSe); δ_C (100 MHz; $CDCl_3$) 15.13 (CH_3CH), 21.48 ((CH_3)$_2$CH), 22.35 ((CH_3)$_2$CH), 25.03 (CH_2), 28.84 (CH), 34.17 (CH), 34.89 (CH_2), 41.10 (CH), 45.20 (CH_2) and 47.84 (CHSe-1); ν_{max} (CH_2Cl_2)/cm^{-1} 2900-2820s (C-H), 1430m (C-CH_3), 1370w (C(CH_3)$_2$), 1350w (C(CH_3)$_2$), 1260m, 1215m, 1160s, 1110m and 1020m; MS (EI) *m/z* 358 (M^+, 19%), 138(57), 123(13), 95(47), 83(100), 69(63), 55(70) and 41(45); $[\alpha]_D^{20}$ -198.4 (c 0.5, $CHCl_3$); (Found: C, 67.00; H, 10.60. $C_{20}H_{38}Se$ requires C, 67.20; H, 10.71%).

Menthyl selenoxide 3

To a solution of menthyl selenide (0.30g, 0.84mmol, 1eq) in CH_2Cl_2 (8ml) was added aqueous hydrogen peroxide (30% w/v, 8.39mmol, 10eq). After stirring at room temperature for 1.5h, H_2O (2ml) was added and the aqueous layer separated and extracted with CH_2Cl_2 (4x2ml). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo* to give the selenoxide (0.31g, 0.82mmol, 98%) as a colourless crystalline solid, mp 62.4-66.5°C, which was used without further purification; δ_H (400 MHz; $CDCl_3$) 0.76 (3H, d, J 6.8 Hz, *Me*CH), 0.84-1.81 (30H, m), 1.98 (1H, dquintet, J 6.8, 2.1 Hz), 2.09 (1H, J 6.6, 2.7 Hz), 2.25 (1H, br.d, J 12.0 Hz), 2.86 (1H, dq, J 11.6, 7.8 Hz, CHSe) and 2.93 (1H, dt, J 12.2, 8.6 Hz, CHSe); ν_{max} (CH_2Cl_2)/cm^{-1} 3000-2820s (C-H), 1430m (C-CH_3), 1370m (C(CH_3)$_2$), 1340m (C(CH_3)$_2$), 1260m, 1220m, 1170s, 1120m, 1030m and 795s (Se=O); MS (EI) *m/z* 374 (M^++1, 4%), 358(M-O, 23), 300(54), 218(20), 160(53), 139(45), 95(35), 83(100), 69(40), 55(45) and 41(30).

Menthyl selenoxide / 2,2,2-trifluoroethane sulfonic acid salt

To a solution of menthyl selenoxide **3** (272mg, 0.73mmol, 1eq) in CH_2Cl_2 (5ml) was added 2,2,2-trifluoroethane sulfonic acid (0.09ml, 0.73mmol, 1eq) and the solution stirred at room temperature for 20min. Concentration *in vacuo* gave the crude salt as a white foam (380mg, 0.71mmol, 97%). Recrystallisation at -30°C gave the menthyl selenoxide / 2,2,2-trifluoroethane sulfonic acid salt as colourless needles, mp 46.2 - 50.2°C (^{n}pentane, diethyl ether); δ_H (400 MHz; $CDCl_3$) 0.78 (3H, d, J 6.8 Hz, *Me*CH), 0.96-1.05 (17H, m), 1.09-1.28 (3H, m), 1.47-1.95 (12H, m), 1.98 (1H, td, J 6.3, 2.2 Hz), 2.27 (1H, app.d, J 11.9 Hz), 3.44

(1H, td, J 11.1, 3.6 Hz, CHSe), 3.64 (2H, q, $^3J(^1H\text{-}^{19}F)$ 9.8 Hz, CH_2CF_3) and 3.84 (1H, td, J 3.5, 12.2 Hz, CHSe); δ_C (100 MHz; $CDCl_3$) 15.55 (CH_3), 21.24 (CH_3), 22.09 (CH_3), 22.15 (CH_3), 24.84 (CH_3), 25.42 (CH_2), 30.54 (CH_3), 30.70 (CH_3), 33.13 (CH_2), 33.45 (CH), 33.58 (CH_2), 33.90 (CH_2), 34.63 (CH_2), 43.97 (CH), 44.92 (CH), 53.04 (CH_2CF_3, q, $^2J(^{13}C\text{-}^{19}F)$ 118.8 Hz), 59.84 (CHSe, t, $^1J(^{13}C\text{-}^{77}Se)$ 138.4 Hz), 64.33 (CHSe, t, $^1J(^{13}C\text{-}^{77}Se)$ 138.4 Hz) and 122.96 (CF_3, q, $^1J(^{13}C\text{-}^{19}F)$ 1099.7 Hz); ν_{max} (CH_2Cl_2)/cm^{-1} 3040-2840s (C-H), 1430m (C-CH_3), 1330 ($C(CH_3)_2$, 1300s, 1210s, 1160s, 1100s and 1000s (Se=O); MS (EI), inconclusive; $[\alpha]_D^{20}$ -154.8° (c 1.5, acetone); (Found: C, 49.10; H, 7.75; S, 5.95. $C_{22}F_3H_{41}O_4SSe$ requires C, 49.15; H, 7.69; S, 5.97%).

Cyclohexyl selenide[21b]

To a suspension of magnesium turnings (10g, excess) in diethyl ether (10ml) was added several crystals of iodine. Cyclohexyl bromide (freshly distilled, bp 72°C/30mmHg) (0.5ml) was then added upon which reaction was seen to occur. The remaining cyclohexyl bromide (18.0ml, 0.15mol, 1eq) was then added as a solution in diethyl ether (175ml) at such a rate so as to maintain gentle reflux. After heating under reflux for 1h, selenium oxychloride (10.0g, 0.06mol, 0.4eq) was added as a solution in diethyl ether (40ml) dropwise. After heating for a further 1h, H_2O (~50ml) was then cautiously added. The aqueous layer was separated and extracted with diethyl ether (4x50ml). The organic layers were then combined, dried ($MgSO_4$) and concentrated *in vacuo*. Distillation of the crude product mixture gave cyclohexyl selenide (7.85g, 0.08mol, 53%) as a pale yellow oil (bp 84°C/0.08mmHg); δ_H (400 MHz; $CDCl_3$) 1.20-1.65 (12H, m, CH_2CH_2), 1.68-1.74 (4H, m, CH_2CH_2), 1.95-2.01 (4H, m, CH_2CH) and 2.90-2.97 (2H,m, CHSe); δ_C (100 MHz; $CDCl_3$) 25.82 (CH_2-4), 26.88 (CH_2-3), 35.13 (CH_2-2) and 37.68 (CH-1, t, $^1J(^{13}C\text{-}^{77}Se)$ 126.32 Hz); ν_{max} (neat)/cm^{-1} 2950-2880s (C-H), 1460m, 1350w, 1270w, 1200m, 1150w, 1070w, 1000m, 920w and 900w; MS (EI) *m/z* 246 (M^+ +1, 20%), 164(19), 83(100), 67(15), 55(76) and 41(52); (Found: C, 58.70; H, 9.15. Calc. for $C_{12}H_{22}Se$: C, 58.77; H, 9.04%).

Cyclohexyl selenoxide 2

Cyclohexyl selenide (266mg, 1.08mmol, 1eq) was dissolved in CH_2Cl_2 (5ml) and saturated aqueous K_2CO_3 (5ml) was added. *m*CPBA (0.34g, 1.08mmol, 1eq) was then added as a slurry in CH_2Cl_2 (20ml) and the reaction left stirring for 70min. Saturated aqueous Na_2CO_3 (15ml) was then added and the aqueous layer extracted with CH_2Cl_2 (3x5ml). The combined organic layers were then dried ($MgSO_4$) and concentrated *in vacuo* to give crude selenoxide **2** (254mg, 0.97mmol, 90%) as a colourless crystalline solid; δ_H (300 MHz; $CDCl_3$) 1.30-1.43 (6H, m, CH_2CH_2), 1.47-1.69 (6H, m, CH_2CH_2), 1.83-2.06 (8H, m, CH_2CH) and 2.83-2.92 (2H, m, CHSe); δ_C (75 MHz; $CDCl_3$) 25.35 (CH_2), 25.61 (CH_2), 26.04 (CH_2), 28.06 (CH_2-2) and 54.40 (CH-1); ν_{max} (thin film)/cm^{-1} 3010-2940s (C-H), 1410s, 1240s and 880s (Se=O); MS (EI) *m/z* 262 (M^+ 5%), 246(M-O, 20%), 164(19), 83(100), 67(10), 55(70) and 41(50).

Cyclohexyl selenoxide /*p*-bromo benzene sulfonic acid salt 7

To a solution of cyclohexyl selenoxide **2** (202mg, 0.77mmol, 1eq) in CH_2Cl_2 (4ml) was added anhydrous *p*-bromobenzene sulfonic acid (183mg, 0.77mmol, 1eq) and the reaction left stirring for 30min. Concentration *in vacuo* gave the crude salt as a white solid (345mg, 0.69mmol, 90%). Recrystallisation gave **7** as colourless needles, mp 96.1-98.4°C (ethyl acetate); δ_H (400 MHz; $CDCl_3$) 1.17-1.42 (6H, m, CH_2CH_2), 1.66 (2H, br d, J 12.7 Hz, CH_2CH_2), 1.71-1.91 (8H, m, CH_2CH_2), 2.00 (2H, br d, J 12.52 Hz, CH_2CH), 2.21 (2H, br d, J 12.52 Hz, CH_2CH), 3.64-3.72 (2H, m, CHSe), 7.51 (2H, d, J 8.6 Hz, ArH) and 7.70 (2H, d, J 8.5 Hz, ArH); δ_C (100 MHz; $CDCl_3$) 24.99 (CH_2), 26.11 (CH_2), 26.47 (CH_2-2 or 6), 28.34 (CH_2-2 or 6), 58.92

(CHSe, t, $^1J(^{13}C\text{-}^{77}Se)$ 145.0 Hz), 124.38 (CAr), 127.64 (CHAr), 131.30 (CHAr) and 143.86 (CAr); ν_{max} (thin film)/cm^{-1} 3000-2800m (C-H), 1420m (SO_2-O), 1210s (SO_2-O), 1160s and 980s (Se=O); MS (EI) inconclusive; (Found: C, 43.2; H, 5.35; S, 6.74. $BrC_{18}H_{27}O_4SSe$ requires C, 43.38; H, 5.46; S, 6.44%). Crystals of quality suitable for X-ray crystallography were obtained by recrystallisation (EtOAc) at -25 °C over several weeks.

Cyclohexyl selenoxide / 2,2,2-trifluoroethane sulfonic acid salt

To a solution of cyclohexyl selenoxide **2** (75.0mg, 0.29mmol, 1eq) in CH_2Cl_2 (3ml) was added 2,2,2-trifluoroethane sulfonic acid (0.03ml, 0.29mmol, 1eq) and the solution was stirred at room temperature for 20min. Concentration *in vacuo* gave the crude salt as a white solid (116mg, 0.27mmol, 95%). Recrystallisation gave cyclohexyl selenoxide / 2,2,2-trifluoroethane sulfonic acid salt as colourless needles, mp 80.6 - 83.3°C (ethyl acetate); δ_H (400 MHz; $CDCl_3$) 1.23-1.49 (6H, m), 1.70 (2H, d, J 12.6 Hz), 1.75-2.04 (8H, m), 2.05 (2H, d, J 12.5 Hz), 2.21 (2H, d, J 12.7 Hz), 3.59 (2H, q, $^3J(^1H\text{-}^{19}F)$ 9.8 Hz, CH_2CF_3) and 3.65-4.14 (2H, m, CHSe); δ_C (100 MHz; $CDCl_3$) 25.00 (CH_2), 26.11 (CH_2), 26.44 (CH_2), 28.23 (CH_2), 53.35 (CH_2CF_3, q, $^2J(^{13}C\text{-}^{19}F)$ 117.5 Hz), 58.93 (CHSe, t, $^1J(^{13}C\text{-}^{77}Se)$ 146.2 Hz) and 122.89 (CF_3, q, $^1J(^{13}C\text{-}^{19}F)$ 1099.8 Hz); ν_{max} (CH_2Cl_2)/cm^{-1} 3000-2800s (C-H), 1560m, 1420m (SO_2-O), 1400m, 1210s (SO_2-O), 1150s, 1110m, 1020m and 1000s (Se=O); MS (EI), inconclusive; (Found: C, 39.60; H, 6.15; S, 7.70. $C_{14}F_3H_{25}O_4SSe$ requires C, 39.53; H, 5.92; S, 7.54%).

Oxidation of prochiral dialkyl sulfides using menthyl selenoxide / 1,1,1-trifluoromethane sulfonic acid (system A) - typical procedure:

To a solution of menthylselenoxide **3** (263mg, 0.70mmol, 1.2eq) in CH_2Cl_2 (8ml) at -25°C was added trifluoromethane sulfonic acid (0.06ml, 0.70mmol, 1.2eq) and the reaction mixture left stirring for 10min. Methyl ^{n}octyl sulfide (0.11ml, 0.59mmol, 1eq) was then added and the reaction left for 24h at -25°C. Saturated aqueous Na_2CO_3 (2ml) was then added to the reaction mixture at -25°C and the reaction allowed to warm to room temperature. The aqueous layer was then separated and extracted with CH_2Cl_2 (3x4ml). The combined organic layers were then dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography [silica gel, petroleum ether (bp 40-60°C) eluant] gave recovered selenide (164mg, 0.46mmol, 65%). Increasing solvent polarity [30% petroleum ether (bp 40-60°C), 50% ethyl acetate, 20% methanol] eluted the sulfoxide (70.0mg, 0.46mmol, 78%) as colourless needles (mp 36.5-38.1°C: lit. 37-38°C[36]).

Oxidation of prochiral dialkyl sulfides using menthyl selenoxide / 2,2,2-trifluoroethane sulfonic acid (system B) - typical procedure:

To a solution of menthyl selenoxide **3** (181mg, 0.49mmol, 1.2eq) in CH_2Cl_2 (5ml) was added 2,2,2-trifluoroethane sulfonic acid (0.06ml, 0.49mmol, 1.2eq). After 10min, methyl ^{n}octyl sulfide (0.08ml, 0.40mmol, 1eq) was added and the reaction stirred at room temperature for 30min. Saturated aqueous Na_2CO_3 (2ml) was then added and the aqueous layer separated and extracted with CH_2Cl_2 (4x2ml). The combined organic extracts were then dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography [silica gel, petroleum ether (bp 40-60°C) eluant] gave recovered selenide (120mg, 0.28mmol, 69%). Increasing eluant polarity (30% petroleum ether (bp 40-60°C), 50% ethyl acetate, 20% ethanol) eluted the sulfoxide (64.0mg, 0.36mmol, 90%) as colourless needles (mp 36.5 - 38.1°C (^{n}pentane): lit. 37-38°C[36]).

Oxidation of prochiral dialkyl sulfides using menthyl selenoxide / (1R)-(-)-camphor-10-sulfonic acid (system C) - typical procedure:

To a solution of menthyl selenoxide **3** (0.20g, 0.53mmol, 1.2eq) in CH_2Cl_2 (3ml) was added (1R)-(-)-camphor-10-sulfonic acid (0.12g, 0.53mmol, 1.2eq) and the mixture cooled to -30°C and stirred for 10min. Methyl ^{n}octyl sulfide (0.080ml, 0.44mmol, 1eq.) was then added and the reaction mixture stirred at -30°C for 1h. Saturated aqueous Na_2CO_3 (4ml) was then added and the reaction mixture allowed to ward to rt. The aqueous layer was then separated and extracted with CH_2Cl_2 (3x3ml). The combined organic layers were then dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by column chromatography [silica gel, hexane eluant] gave the recovered selenide (0.144g, 0.40mmol, 75%). Increasing the solvent polarity [30% hexane, 50% ethyl acetate, 20% methanol] eluted the sulfoxide (0.068g, 0.39mmol, 88%) as colourless needles (mp 36.5-38.1°C: lit. 37-38°C[36]).

Benzyl di^{n}butyl sulfonium trifluoromethane sulfonate

To a solution of benzyl selenoxide **1** (0.32g, 1.17mmol, 1.2eq) in CH_2Cl_2 (10ml) at -25°C was added trifluoromethane sulfonic acid (0.10ml, 1.17mmol, 1.2eq) and the reaction left stirring for 10min. ^{n}Butyl sulfide (0.17ml, 0.97mmol, 1eq) was then added and the reaction left for 48h. Saturated aqueous $NaHCO_3$ (5ml) was then added to the reaction mixture at -25°C and the solution allowed to warm to room temperature. The aqueous layer was then separated and extracted with CH_2Cl_2 (3x4ml). The organic layers were then combined, dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography [silica gel, 10% petroleum ether (40-60°C), 50% ethyl acetate, 40% methanol as eluant] gave benzyl di^{n}butyl sulfonium trifluoromethane sulfonate (188mg, 0.59mmol, 50%). Recrystallisation gave colourless platelets, mp 54 - 57.2°C (diethyl ether); δ_H (300 MHz; $CDCl_3$) 0.89 (6H, t, J 7.2 Hz, CH_2*Me*), 1.38-1.45 (4H, m, CH_2CH_2), 1.61-1.69 (4H, m, CH_2CH_2), 3.38 (4H, t, J 7.5 Hz, CH_2S), 4.80 (2H, s, CH_2Ph), 7.42-7.44 (3H, m, ArH) and 7.50-7.52 (2H, m, ArH); δ_C (100 MHz; $CDCl_3$) 13.05 (CH_3), 21.46 (CH_2), 26.57 (CH_2), 39.61 (CH_2), 45.00 (CH_2), 120.64 (CF_3, q, $^1J(^{13}C\text{-}^{19}F)$ 1273.3 Hz), 127.39 (CAr), 129.54 (ArCH), 129.98 (ArCH), 130.07 (ArCH) and 130.45 (ArCH); ν_{max} (CH_2Cl_2)/cm^{-1} 3050-2870s (C-H), 1600w (C=C),1460m (C=C), 1420m (SO_2-O), 1270s (SO_2-O), 1240s, 1160s, 1050m, 1030s and 900m; MS (EI) inconclusive; (Found: C,49.70; H, 6.50; S, 16.35. $C_{16}F_3H_{25}O_2S_2$ requires C, 49.72; H, 6.52; S, 16.59%).

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