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Formation of dihydroxyselenides from allylic alcohols and their conversion to β-hydroxy epoxides via substitution of a phenylselenonyl group

Matthew A. Cooper[a] and A. David Ward[b,*]

[a]*Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK*
[b]*Department of Chemistry, University of Adelaide, North Terrace, Adelaide, SA 5005, Australia*

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Abstract—Hydroxyselenation of allylic alcohols occurs with high regio- and stereoselectivity to give β,β′-dihydroxyphenylselanyl adducts in high yields. An exception is the reaction of the terminal alcohol, 2-methylprop-2-en-1-ol, which forms only a 1,2-diol product. Generally, the addition is Markovnikov in orientation, but the fact that one *anti*-Markovnikov addition is observed and that addition to 1,2-disubstituted alkenes shows a strong preference for one regioisomer suggests that an interaction of the allylic alcohol with the selenium atom of the reaction intermediate (which weakens the C_β–Se bond in the intermediate) is also an important factor in determining the preference for addition of the phenylselanyl group to the double bond carbon nearest the allylic alcohol. The hydroxyselenated adducts of allylic alcohols can be readily converted to β-hydroxy epoxides in good yields via oxidation with *m*-chloroperbenzoic acid to a selenone and subsequent treatment with base. Hydroxyselenation of crotyl acetate and 3-acetoxycyclohexene is more regiocatholic than hydroxyselenation of the corresponding allylic alcohols. It appears that the known selectivity of additions of phenylselanyl chloride to these acetates in organic solvents is lost when water or a Lewis acid complexes to the acetate group.

1. Introduction

β-Hydroxyselenides are valuable intermediates in organic synthesis[1–4] and have been used for the formation of allylic alcohols,[5,6] C–C bonds[7] and C–N bonds.[1,4,8] They are readily formed in the presence of water from the reaction of epoxides with phenylselenide anion,[9,10] from reduction of α-keto selenides with lithium aluminium hydride,[11] and from reaction of an alkene with either phenylselanyl phthalimide[12,13] or phenylselanyl chloride[14] in the presence of water. The latter hydroxyselenation reactions have not been applied to allylic alcohols.

Liotta and co-workers have reported[15–17] that addition of phenylselanyl chloride in anhydrous organic solvents to cyclic or terminal allylic alcohols occurs in a highly regio- and stereoselective manner, whereas reaction with non-terminal allylic alcohols usually results in the formation of a mixture of regioisomers. We have noted in a preliminary report[18] that hydroxyselenation of allylic alcohols also proceeds with a high degree of regio- and stereo-selectivity. We now report that the hydroxyselenides thus obtained (Scheme 1) can be readily converted into epoxides via oxidation of the selanyl residue with *m*-chloroperbenzoic acid (*m*-CPBA) and subsequent treatment with base.[18,19] This provides a useful route to β-hydroxy epoxides from allylic alcohols (Scheme 1).

2. Results and discussion

2.1. Hydroxyselenation of allylic alcohols

Hydroxyselenation was conducted using phenylselanyl chloride in acetonitrile/water (5:1) solution at room temperature for twenty four hours. The results are summarised in Table 1. For all reactions, except that shown in entry 4, the diol product was predominantly a 1,3-diol. For entries 3, 4 and 8 the regioselectivity corresponds to Markovnikov addition whereas the addition shown in entry 2 is an *anti*-Markovnikov process. This is in contrast to the exclusive formation of Markovnikov adducts upon addition of phenylselanyl halides to similar terminal allylic alcohols in organic solvents at room temperature.[16] For the 1,2-disubstituted alkenes (entries 1, 5, 6, and 7), where the Markovnikov versus *anti*-Markovnikov preferences are less clear cut, the major product corresponds to addition of the phenylselanyl group to the double bond

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* Corresponding author. Tel.: +61-8-8303-5496; fax: +61-8-8303-4358; e-mail address: david.ward@adelaide.edu.au

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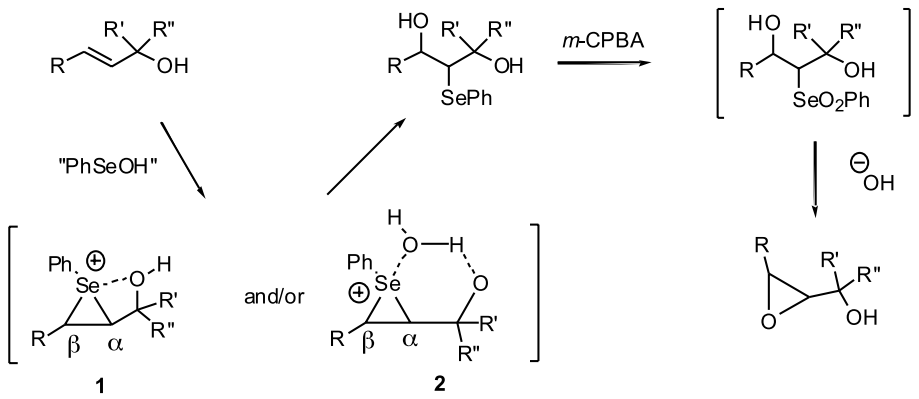
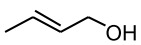
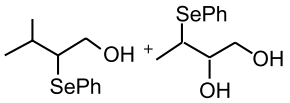
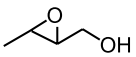
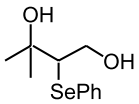
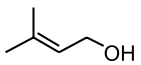
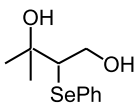
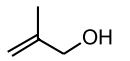
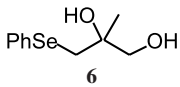
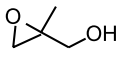
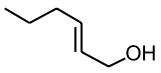
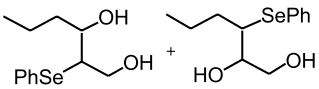
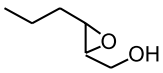
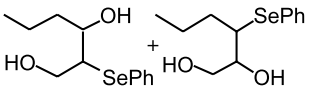
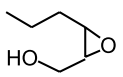
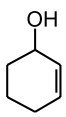
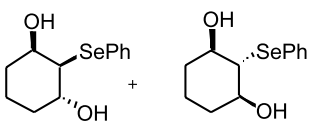
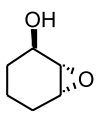
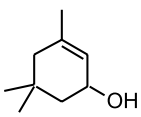
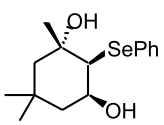
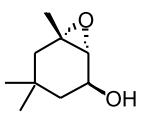


Scheme 1.

Table 1. Hydroxyselenation of allylic alcohols and conversion of the products to epoxides

Entry	Alkene	Addition product	Yield	Epoxide	Yield
1		 **3** (2 : 1) **4**	100	 **43**	66
2		 **5**	86	 **44**	74
3		 **5**	100	 **44**	74
4*		 **6**	85	 **45**	78
5		 **7** (98 : 2) **8**	91	 **46**	70
6		 **9** (9 : 1) **10**	72	 **47**	65
7		 **11** (9 : 1) **12**	91	 **48**	68
8		 **13**	60	 **49**	72

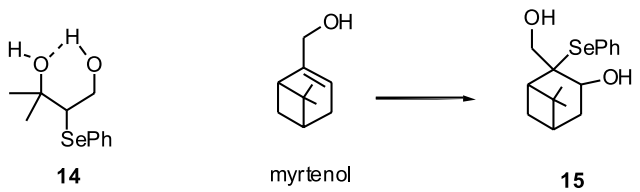
* The structure of the adduct, **6**, in this entry was incorrectly reported in our preliminary report.[18] We thank Dr. D. C. Myles for drawing this to our attention.

carbon nearest to the allylic hydroxyl. This situation is also true for the results shown in entries 2, 3 and 8 but not for that shown in entry 4. We suggest that the dominant formation of 1,3-diol containing products indicates a complexation of the selenium as shown in **1** and/or **2** (Scheme 1) which results in a weakening of the C_β–Se bond that facilitates attack by water at this carbon.

In the addition of phenylselanyl chloride to alkenes in organic solvents it has been noted that the initial *anti*-Markonikov adduct isomerises[20,21] slowly on standing to the Markovnikov adduct. This was not observed in the reaction of the terminal allylic alcohol shown in entry 2, which forms a stable *anti*-Markovnikov product. Hydroxyselenation of the disubstituted alkene, crotyl alcohol, (entry 1), gave a mixture of regioisomers. The disubstituted hex-2-ene-1-ols, (entries 5 and 6), with larger alkyl groups at the β position, exhibited a higher degree of regioselectivity with greater preference for the phenylselanyl group to be located adjacent to the hydroxyl group of the allylic alcohol. The stereochemical course of the addition was found to be *trans*-dominant as hydroxyselenation of *cis*- and *trans*-hex-2-ene-1-ols gave predominantly *threo* (7) and *erythro* (9) adducts, respectively. The possibility that the preference for the formation of 1,3-diols may be due to H-bonding stabilisation[22] (e.g. 14) of a particular adduct was rendered less likely by the observation of ^2J couplings between the hydroxyl protons in the ^{1}H NMR spectra of 5 and 7 (both 1,3-diols) and 10 (a 1,2-diol).

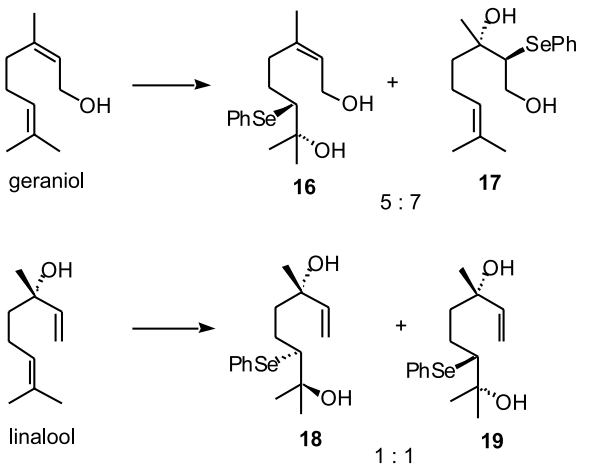
Hydroxyselenation of 2-cyclohexene-1-ol gave a 10:1 mixture of the diastereomers, 11 and 12 in high yield (Table 1). The preferential formation of the product with the *syn* orientation of the original hydroxyl group and the introduced selenium atom can be attributed to an interaction of the lone pair electrons of the oxygen atom with the electron deficient selenium atom as in 1 and/or 2 (Scheme 1).

More substituted cyclic allylic alcohols, such as myrtenol and *cis*-pulegol, gave complex product mixtures, although it was possible to isolate an *anti*-Markovnikov adduct, **15** (Scheme 2), from the reaction with myrtenol. Reaction with isophorol also gave a complex product mixture, however a major product, **13**, corresponding to a Markovnikov addition, crystallised from the mixture on standing (entry 8, Table 1).



Scheme 2.

In order to determine if coordination of the hydroxyl oxygen to the selenium atom of the reagent facilitated delivery to the allylic double bond[16,24] the alcohols geraniol and linalool were subjected to the conditions described above. In both cases no selective hydroxyselenation of the allylic double bond over the isolated double bond was observed, and two products, **16**, **17** and **18**, **19**, respectively, were



Scheme 3.

formed in each case, suggesting that prior complexation of selenium to the allylic hydroxyl group, if it occurs, does not facilitate attack on the double bond compared to attack on the isolated double bond (Scheme 3).

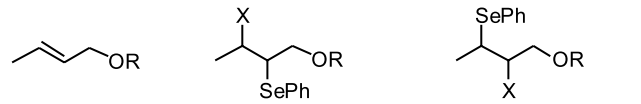
The direction of addition for the major product in the various hydroxyselenations reported above can be summarised as follows. In general the major product is a 1,3-diol, resulting from an interaction of the selenium atom in the reaction intermediate with the oxygen of the allylic alcohol (**1** and/or **2**) that preferentially favours the phenylselanyl group being attached to the double bond carbon nearest to the hydroxyl. This interaction weakens the C_β–Se bond compared to the C_α–Se bond and hence favours attack by the water at the C_β carbon. This direction of addition is only altered when, as in entry 4, electronic factors (attack by the water molecule at a tertiary carbocation or its equivalent of the intermediate episelenonium ion versus attack at a primary carbocation or its equivalent) are sufficient to outweigh this preference. This directing effect of the hydroxyl also explains the isolation of an *anti*-Markovnikov adduct from myrtenol but a Markovnikov adduct from isopulegol, (entry 8).

2.2. Hydroxyselenation of allylic acetates

The addition of phenylselanyl chloride to allylic acetates in organic, non protic, solvents proceeds with a higher degree of regio- and stereoselectivity than addition to the corresponding allylic alcohols in organic solvents.[16] For example, reaction of crotyl acetate, **20**, with phenylselanyl chloride in chloroform gives a mixture of **21** and **22** in the ratio of >20:1. In contrast, using our conditions, hydroxyselenation of **20** gave a mixture of the regioisomers, **23** and **24**, in the ratio 57:43 accompanied by the diols, **3** and **4**, in the ratio 4:1. The diols are presumably formed by in situ hydrolysis of the corresponding acetates, a process that could be enhanced by anchimeric assistance of the neighbouring phenylselanyl group.[24] When the yields are taken into account this represents an overall ratio of 7:3 in favour of selenium addition to the α position for the hydroxyselenation.

The contrasting selectivity of the addition of phenylselanyl chloride to crotyl alcohol and crotyl acetate in organic

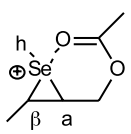
solvents has been attributed to the greater difference between the charge densities at C_α and C_β for crotyl acetate, compared to that of crotyl alcohol.[16] However the enhanced regioselectivity of additions to **20** in organic solvents may also be due to an interaction of the carbonyl group with an electron deficient episelenonium ion intermediate, as in **25**, which promotes selective attack at C_β by weakening the C_β–Se bond. If this were the case, hydroxyselenation of **20** would be more regiocatholic as interaction between the selenonium ion and the carbonyl group would be significantly blocked by a competing hydrogen bonding of the carbonyl oxygen, and, separately, of the positively charged selenium atom, with water. This hypothesis is supported by the fact that the reaction[25–27] of **20** with phenylselanyl chloride in poorer hydrogen bond donor solvents such as methanol, or acetic acid gave only the adducts, **26** and **27**, respectively. Reaction of crotyl trifluoroacetate, **28**, which possesses a more polarised double bond than **20**, with phenylselanyl chloride gave only the single adduct, **29**, in dichloromethane as solvent, and the single adduct, **30**, in methanol as solvent.



20, R = $COCH_3$
28, R = $COCF_3$

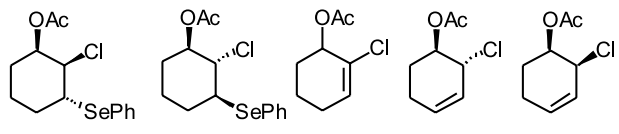
21, X = Cl, R = Ac
23, X = OH, R = Ac
26, X = OMe, R = Ac
27, X = OAc, R = Ac
29, X = Cl, R = $COCF_3$
30, X = OMe, R = $COCF_3$

22, X = Cl, R = Ac
24, X = OH, R = Ac
31, X = OMe, R = Ac

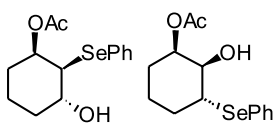


25

Reaction of the cyclic allyl acetate, **32**, with phenylselanyl chloride in deuterochloroform gave a mixture of the stereoisomers, **33** and **34**, in the ratio 9:1 (Scheme 4). The regiochemistry of this addition can be rationalised by invoking an intermediate analogous to **25** so that addition occurs predominately at the *syn* face of the double bond, which in turn suggests that complexation of the selenium with the oxygen of the acetate carbonyl is significant in directing attack to the otherwise more sterically crowded face. The regiochemistry was confirmed, at least for the major product, by an oxidative elimination of the phenylseleno group to give the vinyl chloride, **35** (Scheme 4). Reaction of **32** with phenyl-selanyl chloride in aqueous acetonitrile gave a mixture of **41** and **42** in the ratio 55:45. This result implies that under the conditions of hydroxyselenation there is no neighbouring group participation by the acetate and attack on the double bond, either *syn* or *anti* to the acetate group, is approximately equally likely. The reaction of **32** with phenylselanyl phthalimide and water also proceeds in a regiocatholic manner[23] giving **41** and **42** in a very similar ratio to that described above; surprisingly, it was noted in this paper that addition of water to the reaction of acetoxycyclohexene with phenylselanyl chloride gave only the regioisomer, **33**. However it is likely that the amount of water present in these conditions[23] is very substantially less than the amount used in our general procedure (the amount of water present was not specified in the preliminary communication[23]). If complexation of the acetate with the electron deficient selenium atom in the reaction intermediate or transition state is important in determining the regiochemistry and stereochemistry of the addition reactions to allylic acetates, then addition of a competing coordinating agent, i.e another Lewis acid, should decrease the selectivity described above.



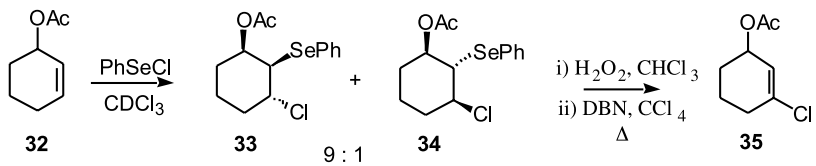
36 **37** **38** **39** **40**



41 **42**

Reaction of **20** with phenylselanyl chloride in deuterochloroform containing zinc chloride gave a mixture of **21** and **22** in the ratio 2:1; in the absence of the Lewis acid **22** was undetected. Whilst complexation of zinc to the carbonyl oxygen should further polarise the double bond, the formation of **22** suggests that the presence of the zinc ion also disrupts an electrostatic interaction between the carbonyl oxygen with the selenonium ion. Methoxyselenation of **20** in the presence of zinc chloride gave a mixture of **26** and **31** in the ratio 7:3; in the absence of the zinc chloride **31** was undetected.

Reaction of **32** with phenylselanyl chloride and zinc chloride in deuterochloroform gave a mixture of the four possible stereoisomers, **33**, **34**, **36** and **37** in the ratio 4:2:2:1. Oxidative elimination of this mixture gave a mixture of the alkenes, **35**, **38**, **39**, and **40** in the ratio 15:5:1.5:1. In the absence of the zinc chloride **36** and **37** were not detected and the ratio of **33**:**34** was 9:1. Thus, in every case, addition of a Lewis acid to the reaction mixture of an allylic acetate with phenylselanyl chloride decreases the regioselectivity, suggesting that addition of an external Lewis acid substantially decreases an intramolecular complexation of



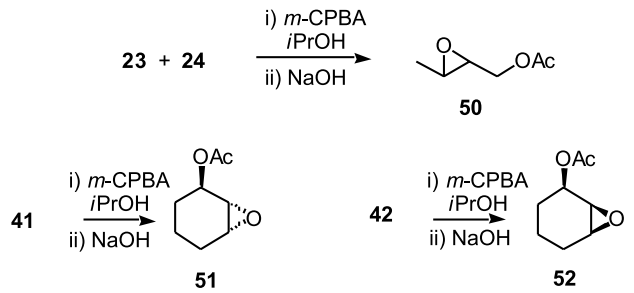
32 **33** 9 : 1 **34** **35**

Scheme 4.

the oxygen of the acetate carbonyl with the electron deficient selenium atom (which is the important factor in the predominance of the major regioisomer). Addition of titanium tetrachloride to the reaction mixture of crotyl alcohol and phenylselanyl chloride in deuterochloroform made no difference to the ratio (7:3) of the regioisomers produced in its absence,[16] showing that the effect is confined to the allylic acetate system.

2.3. Formation of epoxides

The reaction of the hydroxy selenides, obtained from the allylic alcohols shown in Table 1, with excess *m*-CPBA in isopropyl alcohol formed[4,28–31] the corresponding (non-isolated) selenones. In situ treatment of these selenones with aqueous base resulted in the formation of epoxides, **43**–**49**, in good yields (Table 1). Of particular note are the transformations of **11** and **13** to the *trans*-epoxides, **48** and **49**, respectively. Our process provides *trans*-hydroxy epoxides in two steps from the corresponding allylic alcohols, and complements established methodologies which afford *cis*-hydroxy epoxides.[32–34] The epoxide, **48** could be formed in one pot from 2-cyclohexenol by successive treatment with phenylselanyl chloride, *m*-CPBA and sodium hydroxide. The acyclic acetates, **23** and **24**, and the cyclic acetates, **41** and **42**, were also converted cleanly to the corresponding α-acetoxy epoxides by treatment with *m*-CPBA and sodium hydroxide in isopropanol (Scheme 5).



Scheme 5.

2.4. Assignment of stereochemistry

The stereochemistry of **11** was assigned on the basis of the coupling constants observed in this cyclohexyl system (Fig. 1). In **11** H_1 appeared at 4.11 ppm as a multiplet, H_2 at 3.22 ppm as a doublet of doublets (J=2.7, 9.7 Hz) and H_3 at 3.94 as a doublet of triplets (J=4.2, 9.7 Hz) in the ^{1}H NMR spectrum. In **12**, the isosteric and isoelectronic protons H_1 and H_3 were coincident at 3.28 ppm as a doublet of triplets (J=4.2, 10.1 Hz) and H_2 appeared at 2.77 ppm as a triplet (J=10.1 Hz). The COSY45 spectrum of **12** showed that H_2 was coupled only to the resonance at 3.28 ppm and H_1 and H_3 were coupled to a single OH resonance. The stereochemistry of the epoxide, **48**, was assigned as *trans* as H_2 appeared as a doublet (3.0 Hz) coupled to H_3 only. In the *cis*-epoxide, **53**,[34] H_2 appeared as a doublet of doublet of doublets (J=8.0, 5.2, 2.4 Hz), (Fig. 1).

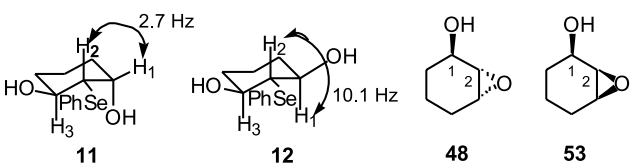


Figure 1.

The regio- and stereochemistry of **13** were assigned from examination of the ^{1}H and ^{13}C NMR, COSY90 and NOESY spectra. H_1 appeared as a triplet of triplets (J=11.3, 3.8 Hz) at 4.28 ppm, which collapsed to a doublet of triplets (J=11.3, 3.8 Hz) at 4.27 ppm upon D_2O exchange (Fig. 2). Thus H_1 was coupled to both the C_1 hydroxyl proton and H_{6a} at 11.3 Hz and to H_2 and H_{6b} at 3.8 Hz. H_2 appeared as a doublet of triplets (J=3.8, 1.8 Hz) at 3.40 ppm, the 1.8 Hz splitting arising from a ^4J coupling to H_{6a}, and the C_1 hydroxyl proton appeared as a doublet (J=11.3 Hz) at 2.49 ppm. The *trans*-epoxide, **48**, showed H_1 at 4.17 ppm as a doublet of doublets (J=7.2, 5.8 Hz) and H_2 at 2.97 ppm and the carbons C_1, C_2 and C_3 at 65.9, 62.9 and 59.4 ppm respectively. The *cis*-epoxide, **53**,[34] (Fig. 2) showed H_1 as a doublet of doublets of doublets (J=11.1, 6.1, 2.0 Hz) at 4.00 ppm, H_2 as a doublet (J=2.0 Hz) at 3.08 ppm and the carbons C_1, C_2 and C_3 at 65.4, 62.2 and 61.0 ppm respectively.

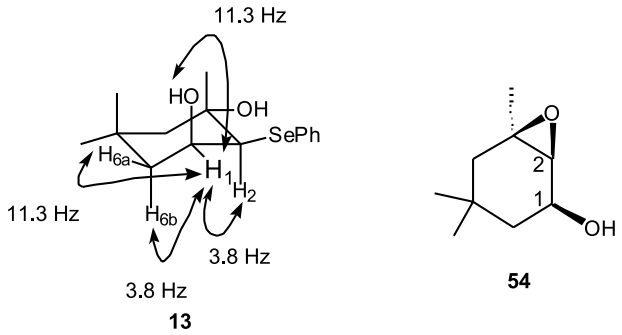


Figure 2.

3. Conclusion

Hydroxyselenation of allylic alcohols occurs readily to give products that result from an addition that is mainly controlled by an interaction of the alcohol group with the selenium atom of the reagent which favours attack by water at the carbon of the double bond remote from the alcohol group. Hydroxyselenation of allylic acetates is much more regiocatholic because the presence of water decreases the complexation of the acetate group and the selenium atom of the reagent which controls the addition of phenylselanyl halides to allylic acetates in organic solvents.

The hydroxyselenated products from allylic alcohols and allylic acetates can be smoothly converted to β-hydroxy epoxides and β-acetoxy epoxides, respectively by treatment of the adduct with *m*-CPBA followed by base. For cyclic allylic alcohols the products are *trans* β-hydroxy epoxides. Our methodology thus complements established direct epoxidation procedures for allylic alcohols that give mainly *cis* β-hydroxy epoxides.

4. Experimental

4.1. General

Infrared spectra were recorded on a Jasco A-102 spectrometer as nujol mulls or liquid films, or as solutions where indicated. ^{1}H NMR, ^{13}C NMR and all two dimensional NMR spectra were obtained at 300 MHz on a Brucker ACP-300 spectrometer using solutions in deuterochloroform with tetramethylsilane as an internal standard unless otherwise specified. Electron impact mass spectra were recorded at 70 eV on an AEI 3074 mass spectrometer. Fast atom bombardment mass spectra and CA-MIKES spectra were recorded on a VG ZAB 2HF mass spectrometer. Melting points were recorded on a Kofler hot-stage apparatus equipped with a Reichert microscope and are uncorrected. Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Flash chromatography was performed using Merck Kieselgel 60 (230–400 mesh) eluting with a gradient of light petroleum/ethyl acetate. Organic extracts were dried over anhydrous sodium sulphate. Phenylselanyl phthalimide was synthesised according to the method of Nicolaou.[12] *m*-CPBA was recrystallised from dichloromethane/light petroleum and was 85% pure as determined by epoxidation of a stoichiometric amount of cyclohexene. As commercially available crotyl alcohol consists of a 70:30 mixture of *trans* and *cis* isomers, reactions using crotyl alchol or crotyl acetate gave a corresponding mixture of *erythro* and *threo* isomers. For clarity only the major *erythro* isomers are quoted.

4.2. General procedure for the hydroxyselenation of the allylic alcohols

To a stirred mixture of the allyl alcohol (5 mmol) in acetonitrile (20 ml) and water (4 ml) was added phenylselanyl chloride (960 mg, 5 mmol). The solution was stirred at room temperature for 24 h, then diluted with saturated sodium bicarbonate (10 ml) and extracted with chloroform (2×30 ml). The combined organic extracts were dried, the solvent removed under reduced pressure and the residue chromatographed to give the compounds or mixtures described below.

4.2.1. 2-Phenylselenobutane-1,3-diol (3) and 3-phenylselenobutane-1,2-diol (4). From crotyl alcohol, as a yellow oil (1.23 g, 100%), bp 135 °C, 0.03 mm, which was an inseparable mixture; [Found: C, 48.7; H, 6.0. $C_{10}H_{14}O_2Se$ requires C, 48.8; H; 5.7%]; ν_{max} (film) 3360, 1050 cm^{-1}; δ_H (**3**) 7.55 (2H, m, Ph), 7.24, (3H, m, Ph), 4.04, (1H, dq, J=7.2, 6.3 Hz, H_3), 3.97 (1H, dd, J=11.7, 4.5 Hz, H_{1a}), 3.80 (1H, dd, J=11.7, 6.5 Hz, H_{1b}), 3.57 (2H, br s, OH), 3.20 (1H, ddd, J=7.2, 6.5, 4.5 Hz, H_2), 1.34 (3H, d, J=6.3 Hz, Me). (**4**): 7.55 (2H, m, Ph), 7.24 (3H, m, Ph), 4.13 (1H, m, H_2), 4.01 (1H, dd, J=11.7, 4.5 Hz, H_{1a}), 3.85 (1H, dd, J=11.7, 6.5 Hz, H_{1b}), 3.57 (2H, s, OH), 3.22 (1H, dq, J=3.3, 6.3 Hz, H_3), 1.33 (3H, d, J=6.3 Hz, Me); *m*/*z* 246 (M), 184 (M−CH_2(OH)CH_2OH), 157 (M−SePh).

4.2.2. 3-Methyl-2-phenylselenobutane-1,3-diol (5). From 3-methyl-2-butene-1-ol, as a colourless oil (1.30 g, 100%), bp 150 °C, 0.05 mm (block); [Found: C, 50.8; H, 6.5. $C_{11}H_{16}O_2Se$ requires C, 51.0; H, 6.2%]; ν_{max} (film) 3300, 1580 cm^{-1}; δ_H 7.59 (2H, m, Ph), 7.28 (3H, m, Ph), 3.95 (2H, m, CH_2O), 3.30, (1H, t, J=5.5 Hz, CHSe), 2.88 (2H, br s, OH), 1.43 (3H, s, Me), 1.41 (3H, s, Me); *m*/*z* 260 (M), 243 (M−OH), 185.

This compound was also obtained from 2-methyl-3-butene-2-ol (1.12 g, 86%).

4.2.3. 2-Methyl-3-phenylselenopropane-1,2-diol (6). From methylallyl alcohol, as a colourless oil. (1.04 g, 85%), bp 138–140 °C, 0.05 mm (block); [Found: C, 49.3; H, 6.0. $C_{10}H_{14}O_2Se$ requires C, 49.0; H, 5.8%]; ν_{max} (film) 3350, 1570, 1470 cm^{-1}; δ_H 7.53 (2H, m, Ph), 7.23, (3H, m, Ph); 3.54 (1H, dd, J=11.1, 5.0 Hz, H_{1a}), 3.47 (1H, dd, J=11.1, 4.5 Hz, H_{1b}), 3.21 (1H, d, J=12.5 Hz, H_{3a}), 3.07 (1H, d, J=12.5 Hz, H_{3b}), 3.03 (1H, s, OH), 2.81 (1H, br dd, J=5.0, 4.5 Hz, OH), 1.22 (3H, s, Me); *m*/*z* 246 (M), 229 (M−OH).

4.2.4. *erythro*-2-Phenylselenohexane-1,3-diol (7) and erythro-3-phenylselenohexane-1,2-diol (8). From *trans*-2-hexene-1-ol, as a yellow oil (1.25 g, 91%), bp 150 °C, 0.06 mm (block) which was an inseparable mixture of (**7**) and (**8**) in the ratio 98:2; [Found: C, 52.8; H, 6.7. $C_{12}H_{18}O_2Se$ requires C, 52.8; H, 6.6%]; ν_{max} (film) 3400, 1575, 1475, 1060, 1020 cm^{-1}; δ_H (**7**) 7.58 (2H, m, Ph), 7.27 (3H, m, Ph), 4.04, (1H, ddd, 11.9, 5.7, 4.5 Hz, H_3), 3.88 (2H, m, $H_{1a}H_{1b}$), 3.29 (1H, dt, J=4.5, 5.2 Hz, H_2), 2.86 (1H, t, J=6.1 Hz, OH), 2.77 (1H, d, J=5.8 Hz, OH), 1.7–1.3, (4H, m, CH_2), 0.92 (3H, t, J=7.3 Hz, Me); *m*/*z* 274 (M), 257 (M−OH), 184 (PhSeCHCH_2), 157 (PhSe).

4.2.5. *threo*-2-Phenylselenohexane-1,3-diol (9) and threo-3-phenylselenohexane-1,2-diol (10). From *cis* 2-hexene-1-ol, as a white solid which was recrystallised (ether/light petroleum) to give the selenide (**9**) as white needles (990 mg, 72%), mp 90–91 °C; [Found: C, 52.8; H, 6.6. $C_{12}H_{18}O_2Se$ requires C, 52.8, H, 6.6%]; ν_{max} (nujol): 3360, 3300, 1580, 1475 cm^{-1}; δ_H 7.58 (2H, m, Ph), 7.25 (3H, m, Ph), 3.91 (3H, m, CHO), 3.30 (1H, dt, J=3.0, 5.3 Hz, H_2), 2.95 (2H, br s, OH), 1.7–1.3 (4H, m, CH_2), 0.90 (3H, t, J=7.2 Hz, Me); *m*/*z* 274 (M), 257 (M−OH), 184 (PhSeCHCH_2), 157 (PhSe). Further elution gave (**10**) as a colourless oil (88 mg, 6%); ν_{max} (film) 3300, 1580, 1480, 1065, 1020 cm^{-1}; δ_H 7.57 (2H, m, Ph), 7.27 (3H, m, Ph), 3.76 (1H, ddt, J=2.9, 5.3, 7.6 Hz, H_2), 3.63 (2H, m, $H_{1a}H_{1b}$), 3.21 (1H, m, H_3), 3.06 (1H, br d, J=2.9 Hz, OH), 2.25 (1H, br t, J=5.3 Hz, OH), 1.68 (2H, m, CH_2) 1.50 (2H, m, CH_2), 0.91 (3H, t, J=6.7 Hz, Me); *m*/*z* 274 (M), 257 (M−OH), 157 (PhSe).

4.2.6. *r*-2-Phenylseleno-*cis*-1,*trans*-3-cyclohexanediol (11) and *r*-2-phenylseleno-*trans*-1,*trans*-3-cyclohexanediol (12). From 2-cyclohexenol (98 mg, 1 mmol) and phenylselanyl chloride (192 mg, 1 mmol) as a yellow oil which was a mixture of the selenides (**11**) and (**12**) (248 mg, 91%), bp 165 °C, 0.03 mm (block) in the ratio 10:1; [Found: C, 53.4; H, 6.1. $C_{12}H_{16}O_2Se$ requires C, 53.14; H, 5.95%); ν_{max} (film) 3400, 1600, 1500, 1095 cm^{-1}; δ_H 7.61 (2H, m, Ph), 7.27 (3H, m, Ph), 4.11 (1H, m, H_1), 3.94 (1H, dt, J=4.2, 9.7 Hz, H), 3.22 (1H, dd, J=2.7, 9.7 Hz, H_2), 2.67 (2H, s, OH), 1.80 (2H, m, CH_2), 1.60 (2H, m, CH_2), 1.40 (2H, m,

CH_2); (**12**) 7.62 (2H, m, Ph), 7.27 (3H, m, Ph), 3.28 (2H, dt, J=4.2, 10.1 Hz, H_1H_3), 3.03 (2H, s, OH), 2.77 (1H, t, J=10.1 Hz, H_2), 1.6–1.2 (6H, m, CH_2); *m/z* 272 (M), 158 [M−(Ph+2OH)], 97 [M−(SePh+OH)].

4.2.7. *r*-2-Phenylseleno-3,5,5-trimethylcyclohexane-*cis*-1,*trans*-3-diol (13). From isophorol as a mixture (960 mg,) from which white crystals of (**13**) formed on standing (670 mg, 42%), mp 103–105 °C; [Found: C, 57.7; H, 7.1. $C_{15}H_{22}O_2Se$ requires C, 57.51; H, 7.08%]; ν_{max} (CCl_4) 3500, 3460, 1475, 1365, 1040 cm^{-1}; δ_H 7.61 (2H, m, Ph), 7.25 (3H, m, Ph), 4.28 (1H, tt, J=11.3, 3.8 Hz, H_1), 4.27 (1H, dt, J=11.3, 3.8, 11.3 Hz, one of the 11.3 couplings disappears with a D_2O shake, H_1), 3.40 (1H, dt, J=3.8, 1.8 Hz, H_2), 2.49 (1H, d, J=11.3 Hz, OH), 1.65 (1H, ddt, J=11.4, 3.8, 1.8 Hz, H_{6e}), 1.52 (1H, d, J=14.6 Hz, H_{4a}), 1.48 (3H, s, Me), 1.38 (1H, dt, J=14.6, 1.8 Hz, H_{4e}), 1.32 (1H, s, OH), 1.14 (3H, s, Me), 1.13 (1H, dd, J=11.4, 11.3 Hz, H_{6a}), 0.95 (3H, s, Me); δ_C 143.8, 134.0, 129.3, 127.6 (Ar), 76.4 (C_3), 68.1 (C_1), 65.6 (C_2), 46.8 (C_4), 45.8 (C_6), 33.6 (Me), 31.8 (Me), 28.2 (Me); *m/z* 314 (M), 297 (M−OH), 139 [M−(SePh+H_2O)], 121 [M−(SePh+$2H_2O$)].

4.2.8. 2-Hydroxymethyl-2-phenylseleno-3-hydroxy-6,6-dimethyl-bicyclo[3.3.1]-heptane (15). From (1*R*)(−) myrtenol, as a complex mixture from which it was possible to isolate the selenide (**15**) by chromatography as an oil (216 mg, 13%); ν_{max} (film) 3360, 1580, 1480, 1375, 1160, 1020, 740 cm^{-1}; δ_H 7.61 (2H, m, Ph), 7.28 (3H, m, Ph), 4.36 (1H, d, J=12.6 Hz, CH_aOH), 4.10 (1H, m, C*H*OH), 4.19 (1H, d, J=12.6 Hz, CH_bOH), 2.2–1.6 (6H, m), 2.0 (2H, br s, OH), 1.20 (3H, s, Me), 1.18 (3H, s, Me); *m/z* 326 (M), 309 (M−OH), 232 [M−(OH+Ph)], 151 (M−(OH+SePh)], 42 (CMe_2); HRMS (EI): M^+, found 326.0796. $C_{16}H_{22}O_2Se$ requires 326.0785.

4.2.9. 3(*S),7-Dimethyl-2(*S**)-phenylselenooct-6-ene-1,3-diol (17) and 3,7-dimethyl-6-phenylselenooct-2-ene-1,7-diol (16).** From geraniol (308 mg, 2 mmol) as a yellow oil which was an inseparable mixture of (**17**) and (**16**) in the ratio 7:5 (400 mg, 62%); ν_{max} (film) 3350, 1580, 1480, 1040 cm^{-1}; δ_H (**17**) 7.60 (2H, m, Ph), 7.25 (3H, m, Ph), 5.20 (1H, t, J=6.7 Hz, H_6), 4.03 (1H, m, H_{1a}), 4.02, (1H, m, H_{1b}), 3.07 (1H, m, H_2), 2.76 (2H, s, OH), 2.43 (1H, m, H_{5a}), 2.20 (1H, m, H_{5b}), 1.8–1.6 (2H, m, H_4), 1.51 (3H, s, Me), 1.35 (3H, s, Me) 1.24 (3H, s, Me); (**16**) 7. 57 (2H, m, Ph), 7.24 (3H, m, Ph), 5.09 (1H, t, J=6.8 Hz, H_2), 4.10 (2H, dd, J=15.0, 6.8 Hz, $H_{1a}H_{1b}$), 3.60 (1H, m, H_6), 2.47 (2H, br s, OH), 2.1–1.9 (4H, m, CH_2), 1.67 (3H, s, Me), 1.59 (3H, s, Me), 1.27 (3H, s, Me); *m/z* 328 (M), 154 [M−(SePh+OH)]; HRMS (EI): M^+, found 328.0938. $C_{16}H_{24}O_2Se$ requires 328.0941.

4.2.10. 2,6(*S)-Dimethyl-3(*R**)-phenylseleno-oct-7-ene-2,6-diol (18) and 2,6(*S**)-dimethyl-3(*S**)-phenylselenoct-7-ene-2,6-diol (19).** From linalool (308 mg, 2 mmol) as a yellow oil which was an inseparable mixture of **18** and **19** in the ratio 1:1 (140 mg, 42%); ν_{max} (CCl_4) 3360, 1580, 1480, 1370, 1040 cm^{-1}; δ_H (**18**) 7.57 (2H, m, Ph), 7.26 (3H, m, Ph), 6.80 (1H, dd, J=17.4, 10.7 Hz, H_x), 5.22 (1H, dd, J=17.4, 1.2 Hz, H_a), 5.03 (1H, dd, J=10.7, 1.2 Hz, H_b), 3.35, (1H, m, CHSe), 3.2 (2H, br s, OH), 2.2–1.4 (4H, m, CH_2), 1.39 (3H, s, Me), 1.31 (3H, s, Me), 1.27 (3H, s, Me); (**19**) 7.57 (2H, m, Ph), 7.26 (3H, m, Ph), 5.90 (1H, dd, J=17.4, 10.7 Hz, H_x), 5.14 (1H, dd, J=17.4, 1.2 Hz, H_a), 4.99 (1H, dd, J=10.7, 1.2 Hz, H_b), 3.2 (2H, br s, OH), 2.65 (1H, m, CHSe), 2.2–1.4 (4H, m, CH_2), 1.37, 3H, s, Me), 1.33 (3H, s, Me), 1.28 (3H, s, Me); m/s 328 (M), 171 [M−(SePh+OH)], 127 [M−(SePh+OH+CH=CH_2)]; HRMS (EI): M^+, found 328.0963. $C_{16}H_{24}SeO_2$ requires 328.0942.

4.2.11. Reactions of crotyl acetate (20). *Using the above general procedure*. 3-Hydroxy-2-phenylselenobutyl acetate (**23**) and 2-hydroxy-3-phenylselenobutyl acetate (**24**) were prepared from crotyl acetate, using the general procedure, as a yellow oil (460 mg, 32%), bp 145 °C, 0.05 mm (block) which was an inseparable mixture in the ratio 57:43 (**23**:**24**); ν_{max} (film) 3350, 1720, 1560, 1030 cm^{-1}; δ_H (**24**) 7.59 (2H, m, Ph), 7.27 (3H, m, Ph), 4.19 (2H, m, CH_2OAc), 3.87 (1H, m, CHOH), 3.44 (1H, dq, J=4.7, 7.0 Hz, CHSe), 2.60 (1H, br d, J=4.1 Hz, OH), 2.05 (3H, s, COMe), 1.43 (3H, d, J=7.0 Hz, Me); (**23**) 7.59 (2H, m, Ph), 7.27 (3H, m, Ph), 4.20 (2H, m, CH_2OAc), 3.68 (1H, m, CHO), 3.55 (1H, m, CHSe), 2.74 (1H, br s, OH), 2.06 (3H, s, COMe), 1.46 (3H, d, J=6.8 Hz, Me); *m/z* 288 (M), 245 (M−Ac), 131 (M−SePh); HRMS (EI): M^+, found 288.0253. $C_{12}H_{16}O_3Se$ requires 288.0264.

Further elution gave a mixture of (**3**) and (**4**), in the ratio 4:1, as a colourless oil (455 mg, 37%).

With phenylselanyl chloride in methanol. To crotyl acetate (114 mg, 1 mmol) in dry methanol (10 ml) under nitrogen was added phenylselanyl chloride (191 mg, 1 mmol) and the reaction was stirred at room temperature for 18 h. The solvent was removed under reduced pressure and the residue chromatographed to give 3-methoxy-2-phenylselenobutyl acetate (**26**) as a light yellow oil (260 mg, 86%); ν_{max} (film) 1730, 1580, 1480, 1125, 1100, 700 cm^{-1}; δ_H 7.57 (2H, m, Ph), 7.25 (3H, m, Ph), 4.43 (1H, dd, J=11.7, 4.5 Hz, H_{1a}), 4.36 (1H, dd, J=11.7, 6.4 Hz, H_{1b}), 3.62 (1H, qn, J=6.1 Hz, H_3), 3.49 (1H, dt, J=4.6, 6.1 Hz, H_2), 3.35 (3H, s, OMe), 1.97 (3H, s, COMe), 1.34 (3H, d, J=6.1 Hz, Me); *m/z* 302 (M), 242 (M−OAc), 184 (M−{OAc+[CH_3CH(OMe)]}), 157 (SePh), 85; HRMS (EI): M^+, found 302.0423. $C_{13}H_{18}O_3Se$ requires 302.0421.

With phenylselanyl chloride and zinc chloride in methanol. To a stirred mixture of crotyl acetate (114 mg, 1 mmol) and zinc chloride (136 mg, 1 mmol) in dry methanol (10 ml) under nitrogen was added phenylselanyl chloride (191 mg, 1 mmol). The mixture was stirred at room temperature for 18 h, the solvent removed under reduced pressure and the residue chromatographed to give a mixture of 3-methoxy-2-phenylselenobutyl acetate (**26**) and 2-methoxy-3-phenylselenobutyl acetate (**31**) in the ratio 7:3 as a yellow oil (83 mg, 27%); δ_H (**31**) 7.60 (2H, m, Ph), 7.26, (3H, m, Ph), 4.39 (2H, m, $H_{1a}H_{1b}$), 3.64, (1H, dt (J=6.3, 6.1 Hz), H_2), 3.47 (1H, m, H_3), 3.33 (3H, s, OMe), 1.98 (3H, s, COMe), 1.37, (3H, d J=6.1 Hz, Me).

With phenylselanyl bromide in acetic acid. A mixture of crotyl acetate (114 mg, 1 mmol), phenylselanyl bromide (236 mg, 1 mmol) and anyhdrous sodium acetate (330 mg, 4 mmol) in glacial acetic acid (10 ml) was stirred at room

temperature for 24 h. The solution was diluted with water (20 ml) then extracted with ethyl acetate (2×20 ml). The combined organic extracts were washed with water (20 ml), 10% sodium bicarbonate, dried, the solvent removed under reduced pressure and the residue chromatographed to give 3-acetoxy-2-phenylselenobutyl acetate (**27**) as a yellow oil (170 mg, 52%); ν_{max} (film) 1740, 1375, 1220, 1020, 690 cm^{-1}; δ_H 7.59 (2H, m, Ph), 7.27 (3H, m, Ph), 5.19 (1H, qn, *J*=5.9 Hz, CHOAc), 4.41 (1H, dd, *J*=11.7, 5.7 Hz, CH_aOAc), 4.29 (1H, dd, *J*=11.7, 7.1 Hz, CH_bOAc), 3.51 (1H, dt, *J*=7.1, 5.7 Hz, CHSe), 2.02 (3H, s, Me), 1.96 (3H, s, Me), 1.37 (3H, d, *J*=6.0 Hz, Me); *m/z* 330 (M), 271 (M−OAc), 173 (M−SePh); HRMS (EI): M^+, found 330.0363. $C_{14}H_{18}O_4Se$ requires 330.0369. Further elution gave the alcohol (**23**) as a yellow oil (34 mg, 12%).

With phenylselanyl chloride. To a solution of crotyl acetate (11.4 mg, 0.1 mmol) in deuterochloroform (0.5 ml) was added phenylselanyl chloride (19.1 mg, 0.1 mmol) and the reaction followed by ^1H NMR. Only the adduct 3-chloro-2-phenylselenobutyl acetate (**21**) was detected; δ_H 7.61 (2H, m, Ph), 7.30, (3H, m, Ph), 4.49 (2H, d, *J*=5.6 Hz, CH_2O), 4.37 (1H, m, CHCl), 3.47 (1H, dt, *J*=6.8, 5.5 Hz, CHSe), 2.03 (3H, s, Me), 1.67 (3H, d, *J*=6.6 Hz, Me).

With phenylselanyl chloride and zinc chloride. To a stirred mixture of crotyl acetate (114 mg, 1 mmol) and anhydrous zinc chloride (136 mg, 1 mmol) in deuterochloroform (2 ml) under nitrogen was added phenylselanyl chloride (191 mg, 1 mmol) in deuterochloroform (1 ml). ^1H NMR showed a mixture of the adducts (**21**) and (**22**) in the ratio 2:1; δ_H (**22**) 7.61 (2H, m, Ph), 7.30 (3H, m, Ph), 4.43 (2H, d, *J*=5.8 Hz, CH_2OAc), 4.31 (1H, m, CHCl), 3.23 (1H, m, CHSe), 2.10 (3H, s, COMe), 1.58 (3H, d, *J*=7.2 Hz, Me).

4.2.12. 3-Methoxy-2-phenylselenobutyl trifluoroacetate (30). To a stirred mixture of the trifluoroacetate (**28**) (169 mg, 1 mmol) in dry methanol (10 ml) under nitrogen was added phenylselanyl chloride (191 mg, 1 mmol). The mixture was stirred at room temperature overnight, the solvent removed under reduced pressure and the residue chromatographed to give the selenide (**30**) as a yellow oil (140 mg, 78%); ν_{max} (film) 1750, 1580, 1440, 1100, 695 cm^{-1}; δ_H 7.58 (2H, m, Ph), 7.28 (3H, m, Ph), 5.12 (2H, d, *J*=5.8 Hz, CH_2O), 4.30 (1H, m, CHO), 3.58 (1H, dt, *J*=7.0, 5.6 Hz, CHSe). 1.63 (3H, d, *J*=6.3 Hz, Me); *m/z* 274 (M−$COCF_3$), 184 (PhSeCH), 85 ($COCF_3$).

4.2.13. 3-Chloro-2-phenylselenobutyl trifluoroacetate (29). To crotyl trifluoroacetate (85 mg, 0.5 mmol) in deuterochloroform (2 ml) under nitrogen was added phenylselanyl chloride (96 mg, 0.5 mmol) and the reaction was followed by ^1H NMR Only the adduct (**29**) could be detected; δ_H 7.58 (2H, m, Ph), 7.28 (3H, m, Ph), 5.12 (2H, d, *J*=5.8 Hz, CH_2O), 4.30 (1H, m, CHCl), 3.58 (1H, dt, *J*=7.0, 5.6 Hz, CHSe), 1.63 (3H, d, *J*=6.7 Hz, Me).

4.2.14. Reactions of acetoxycyclohex-2-ene (32). *With phenylselanyl chloride*. To a stirred mixture of the acetate (**32**) (70 mg, 0.5 mmol) in deuterochloroform (2 ml) under nitrogen was added phenylselanyl chloride (96 mg, 0.5 mmol) and the mixture stirred at room temperature for 2 h. ^1H NMR showed a mixture of (**33**) and (**34**) in the ratio 9:1; δ_H (**33**) 7.58 (2H, m, Ph), 7.28 (3H, m, Ph), 5.33 (1H, dt, *J*=4.1, 7.8 Hz {collapses to dd, *J*=4.1, 7.8 Hz, upon irradiation at 3.8 ppm}, CHO), 4.50 (1H, m, {collapses to t, *J*=4.1 Hz, upon irradiation at 3.8 ppm}, CHCl), 3.81 (1H, m,{collapses to d, *J*=2.4 Hz, upon irradiation at 5.3 and to d, *J*=4.1 Hz, upon irradiation at 4.5 ppm}, CHSe), 2.26 (2H, m), 1.98 (3H, s, Me), 1.75 (4H, m); (**34**) 7.58 (2H, m, Ph), 7.28 (3H, m, Ph), 4.83 (1H, ddd, *J*=9.4, 9.4, 4.4 Hz, {collapses to dd, *J*=4.4, 9.4, upon irradiation at 3.2 ppm}, CHO), 3.70 (1H, m, CHCl), 3.20 (1H, t, *J*=9.4 Hz, {collapses to d, *J*=9.4 Hz, upon irradiation at 4.8 or 3.7 ppm}, CHSe), 2.26 (2H, m), 2.06 (3H, s, Me), 1.75 (4H, m).

With phenylselanyl chloride and zinc chloride. To a stirred mixture of the acetate (**32**) (70 mg, 0.5 mmol) and anyhdrous zinc chloride (68 mg, 0.5 mmol) in deutero-chloroform (2 ml) under nitrogen was added phenylselanyl chloride (96 mg, 0.5 mmol) and the mixture stirred at room temperature for 2 h. ^1H NMR showed a mixture of (**33**), (**34**), (**36**) and (**37**) in the ratio 4:2:2:1; δ_H (**36**) 7.58 (2H, m, Ph), 7.28 (3H, m, Ph), 5.51 (1H, ddd, *J*=9.4, 3.1, 3.1 Hz, CHO), 4.36 (1H, m, CHCl), 3.68 (1H, m, H_3), 2.26 (2H, m), 2.10 (3H, s, Me), 1.75 (4H, m); (**37**) 7.58 (2H, m, Ph), 7.28 (3H, m, Ph), 4.64 (1H, dt, *J*=4.1, 8.0 Hz, CHO), 4.58 (1H, m, CHCl), 3.67 (1H, m, CHSe), 2.26 (2H, m), 2.11 (3H, s, Me), 1.75 (4H, m).

4.2.15. Acetoxy-3-chlorocyclohex-2-ene (35). A mixture of the acetate, (**32**), (280 mg, 2 mmol) and phenylselanyl chloride (420 mg, 4.2 mmol) in dry chloroform (20 ml) was stirred at room temperature for 1 h. Hydrogen peroxide (34% v/v, 5 ml) was then added and the mixture stirred vigorously for a further 20 min. The solution was washed with water (10 ml), dried and the solvent removed under reduced pressure. The residue was redissolved in carbon tetrachloride (5 ml) and added to a refluxing mixture of DBN (620 mg, 5 mmol) in carbon tetrachloride (20 ml) under nitrogen. The mixture was refluxed for 15 min. then the cooled solution was washed with 10% hydrochloric acid (10 ml), water (10 ml), dried, the solvent removed under reduced pressure and the residue chromatographed to give the alkene[35] (**35**) as a colourless liquid (150 mg, 43%); ν_{max} (CCl_4) 1735, 1650, 1240 cm^{-1}; δ_H 5.90 (1H, dt, *J*=4.3, 1.6 Hz, H_2), 5.27 (1H, m, H_1), 2.33 (2H, m), 2.03 (3H, s, Me), 1.8–1.7 (4H, m); *m/z* 174/176 (weak, M), 139 (M−Cl), 114/116 (M−HOAc), 96 [M−(Cl+Ac)], 79 [M−(Cl+HOAc)].

4.2.16. Acetoxy-2-chlorocyclohex-2-ene (38), *trans* acetoxy-2-chlorocyclohex-3-ene (39) and *cis* acetoxy-2-chlorocyclohex-3-ene (40). The reaction was carried out as for the preparation of (**35**) above, except anhydrous zinc chloride (272 mg, 2 mmol) was added to the initial reaction mixture. Chromatography gave an inseparable mixture of (**35**), (**38**), (**39**) and (**40**) in the ratio 15:5:1.5:1; δ_H (**38**) 7.58 (2H, m, Ph), 7.24 (3H, m, Ph), 6.11 (1H, dd, *J*=3.3, 4.9 Hz, H_3), 5.35 (1H, m, H_1), 2.33 (2H, m), 2.10 (3H, s, Me), 1.8–1.7 (4H, m); (**39**) 7.58 (2H, m, Ph), 7.24 (3H, m, Ph), 5.9–5.7 (2H, m, CHX), 5.02 (1H, dt, *J*=11.6, 3.7 Hz, H_1), 4.78 (1H, m, H_2), 2.33 (2H, m), 2.12 (3H, s, Me), 1.8–1.7 (4H, m); (**40**) 7.58 (2H, m, Ph), 7.24 (3H, m, Ph), 5.9–5.7 (2H, m, CHX), 5.10 (1H, ddd, *J*=3.0, 3.5, 8.0 Hz,

H_1), 4.68 (1H, m, H_2), 2.33 (2H, m,), 2.08 (3H, s, Me), 1.8–1.7 (4H, m).

4.2.17. *r*-2-Phenylseleno-*trans*-3-hydroxycyclohexane-*cis*-1-acetate (41) and *r*-2-hydroxy-*trans*-3-phenylseleno-cyclohexane-*cis*-1-acetate (42). To a stirred mixture of the acetate (**32**) (910 mg, 6.5 mmol) in acetonitrile (20 ml) and water (5 ml) at 0 °C was added a solution of phenylselanyl chloride (1.25 g, 6.5 mmol) in acetonitrile (3 ml). The mixture was stirred at 0 °C for 1 h, then at room temperature for 24 h. The solution was then diluted with saturated sodium bicarbonate (10 ml) and extracted with chloroform (3×20 ml). The combined organic extracts were washed with saturated sodium chloride (10 ml), dried, the solvent removed under reduced pressure and the residue chromatographed to give the selenide (**41**) (955 mg, 47%) as a yellow oil, bp 150 °C, 0.05 mm (block); ν_{max} (film) 3350, 1720, 1580, 1480 cm^{-1}. δ_H 7.60 (2H, m, Ph), 7.28 (3H, m, Ph), 5.43 (1H, m, CHOAc), 4.12 (1H, m, CHOH), 3.47 (1H, dd, *J*=7.7, 3.3 Hz, CHSe), 2.84 (1H, br s, OH), 1.90 (3H, s, Me), 2.1–1.4 (6H, m); δ_C 170.1 (C=O), 135.0 134.7 129.8 123.7 (Ar), 73.6 (*C*OAc), 70.8 (COH), 55.6 (CSe), 33.0, 21.5, 20.8, 19.7; *m/z* 314 (M), 271 (M−Ac), 157 (M−SePh), 147, 104, 76. Further elution gave the selenide (**42**) (775 mg, 38%) as a yellow oil; δ_H 7.60 (2H, m, Ph), 7.28 (3H, m, Ph), 5.30 (1H, m, CHOAc), 3.52 (1H, dd, *J*=9.5, 2.7 Hz, CHOH), 3.39 (1H, dt, *J*=9.6, 3.7 Hz, CHSe), 2.61 (1H, br s, OH), 2.11 (3H, s, Me), 2.1–1.4 (6H, m); δ_C 170.7 (C=O), 136.2 134.2 129.0 128.3 (Ar), 72.3 (*C*OAc), 71.8 (COH), 46.3 (CSe), 31.4, 28.2, 21.2, 20.9.

4.3. General procedure for the conversion of selenides to epoxides

The selenide, or mixture of selenides (1 mmol), *m*-CPBA (1.01 g 85%, 5 mmol) and 10% potassium hydroxide (2 ml) in isopropyl alcohol (20 ml) was stirred at room temperature for 1 h. The solution was diluted with saturated sodium thiosulfate (10 ml) and extracted with chloroform (2×20 ml). The combined organic extracts were washed with 10% sodium hydroxide (10 ml), dried, the solvent removed under reduced pressure and the residue chromatographed.

By this means the following epoxides were prepared:

4.3.1. *trans*-2,3-Epoxybutan-1-ol (43).[36] From the mixture of selenides (**3**) and (**4**), as a colourless oil (58 mg, 66%); ν_{max} (film) 3460, 1580, 1440, 1235 cm^{-1}; δ_H 4.01 (1H, br s, OH), 3.94 (1H, dd, *J*=12.7, 2.4 Hz, H_{1a}), 3.63 (1H, dd, *J*=12.7, 4.4 Hz, H_{1b}), 3.06 (1H, dq, *J*=2.4, 5.3 Hz, H_3), 2.93 (1H, dt, *J*=4.5, 2.4 Hz, H_2), 1.35 (3H, d, *J*=5.3 Hz, Me).

4.3.2. 3,4-Epoxy-2-methyl-butan-2-ol (44).[37] From the selenide (**5**), as a colourless oil (75 mg, 74%); ν_{max} (film) 3320, 1580, 1030 cm^{-1}; δ_H 3.98 (1H, br s, OH), 3.86 (1H, dd, *J*=12.2, 4.2 Hz, H_{1a}), 3.68 (1H, dd, *J*=12.2, 6.9 Hz, H_{1b}), 3.01 (1H, dd, *J*=6.9, 4.2 Hz, H_2), 1.36 (3H, s, Me), 1.32, (3H, s, Me).

4.3.3. 2,3-Epoxy-2-methylpropan-1-ol (45).[38] From the selenide (**6**), as a colourless oil (69 mg, 78%); ν_{max} (film) 3340, 1580, 1030 cm^{-1}; δ_H 3.73 (1H, d, *J*=12.3 Hz, H_{1a}), 3.62 (1H, d, *J*=12.3 Hz, H_{1b}), 2.92 (1H, d, *J*=4.8 Hz, H_{3a}), 2.66 (1H, d, *J*=4.8 Hz, H_{3b}), 1.37 (3H, s, Me).

4.3.4. *trans*-2,3-Epoxyhexan-1-ol (46).[39] From the selenide (**7**), as a colourless oil (75 mg, 65%); ν_{max} (film) 3430, 1255, 1030 cm^{-1}; δ_H 4.07 (1H, br s, OH), 3.78 (1H, dd, *J*=12.8, 3.0 Hz, H_{1a}), 3.68 (1H, dd, *J*=12.8, 6.7 Hz, H_{1b}), 2.96 (2H, m, H_2 and H_3), 1.6–1.3, (4H, m, CH_2), 0.95 (3H, t, *J*=7.5 Hz, Me).

4.3.5. *cis*-2,3-Epoxyhexan-1-ol (47).[40] From the selenide (**9**), as a colourless oil (81 mg, 70%); ν_{max} (film) 3430, 1255, 1030 cm^{-1}; δ_H 4.09 (1H, br s, OH), 3.85 (1H, dd, *J*=12.8, 2.4 Hz, H_{1a}), 3.53 (1H, dd, *J*=12.8, 4.2 Hz, H_{1b}), 2.89 (2H, m, H_2 and H_3), 1.5–1.3 (4H, m, CH_2), 0.89 (3H, t, *J*=7.3 Hz, Me).

4.3.6. *trans*-2,3-Epoxycyclohexan-1-ol (48).[41] From the selenide (**11**), as a colourless oil (79 mg, 70%); ν_{max} (CCl_4) 3620, 1230, 825 cm^{-1}; δ_H 4.02 (1H, m, H_1), 3.24 (1H, m, H_3), 3.08 (1H, d, *J*=3.0 Hz, H_2), 2.19 (1H, br d, *J*=4.3 Hz, OH), 2.0–1.7 (3H, m), 1.5–1.2 (3H, m); *m/z* 97 (M−OH), 70 (M−C_2H_4O), 57 (M−$C_2H_5O_2$).

This compound was also formed from a mixture of 2-cyclohexenol (98 mg, 1 mmol) in acetonitrile (20 ml) and water (4 ml) to which was added phenylselanyl chloride (191 mg, 1 mmol) and the mixture stirred at room temperature for 18 h. A solution of *m*-CPBA (1.01 g, 5 mmol) in isopropyl alcohol (10 ml) and 10% aqueous potassium hydroxide (2 ml) was then added and the mixture stirred at room temperature for a further hour. Work up as described in the general procedure gave the epoxide (**48**) (70 mg, 62%).

4.3.7. *trans*-2,3-Epoxy-3,5,5-trimethylcyclohexan-1-ol (49).[42] From the selenide (**13**), (31 mg, 0.1 mmol) as a colourless oil (11 mg, 72%); ν_{max} (CCl_4) 3325, 1360, 1040 cm^{-1}: δ_H 4.17 (1H, dd, *J*=7.2, 5.8 Hz, H_1), 2.97 (1H, s, H_2), 2.15 (1H, br s, OH), 1.71 (1H, d, *J*=15.1 Hz, H_{4a}), 1.64 (1H, dd, *J*=13.4, 5.8 Hz, H_{6a}), 1.52 (1H, d, *J*=15.1 Hz, H_{4b}), 1.34 (3H, s, Me), 1.17 (1H, dd, *J*=13.4, 7.2 Hz, H_{6b}), 0.97 (3H, s, Me), 0.91 (3H, s, Me); δ_C 65.9 (C_1), 62.9 (C_2), 59.4 (C_3), 42.5 (C_4), 42.4 (C_6), 31.6 (Me), 28.9 (C_5), 28.5 (Me), 24.1 (Me).

4.3.8. 2,3-Epoxy-1-butyl acetate (50).[43] From a mixture of the selenides (**23**) and (**24**), as a colourless oil (92 mg, 71%); ν_{max} (film) 3460, 1720, 1580, 1230, 1030 cm^{-1}; δ_H 4.37 (1H, dd, *J*=12.2, 3.0 Hz, H_{1a}), 3.92 (1H, dd, *J*=12.2, 6.1 Hz, H_{1b}), 2.94 (2H, m, CH_2), 2.10 (3H, s, COMe), 1.35 (3H, d, *J*=5.0 Hz, Me).

4.3.9. *trans*-2,3-Epoxycyclohexane-1-acetate (51).[44] From the selenide (**41**), as a colourless oil (52 mg, 67%); ν_{max} (film) 1725, 1370, 1245 cm^{-1}; δ_H 5.04 (1H, dt, *J*=1.2, 6.8 Hz, H_1), 3.29 (1H, m, H_3), 3.23, (1H, m, H_2), 2.11 (3H, s, Me), 1.8–1.3 (6H, m).

4.3.10. *cis*-2,3-Epoxycyclohexane-1-acetate (52).[44] From the selenide (**42**), as a colourless oil (57 mg, 73%); ν_{max} (film) 1725, 1370, 1240 cm^{-1}; δ_H 5.12 (1H, dt, *J*=1.4

5.2 Hz, H_1), 3.29 (1H, m, H_3), 3.07 (1H, d, J=3.6 Hz, H_2), 2.10 (3H, s, Me), 1.8–1.3 (6H, m).

4.3.11. *cis*-2,3-Epoxycyclohexan-1-ol (53). This compound was prepared by the method of Magnusson[34] from 2-cyclohexenol (196 mg, 2 mmol) and gave the epoxide (**54**) (155 mg, 68%) as a colourless oil; ν_{max} (CCl_4) 3590, 1230, 820 cm^{-1}. δ_H 4.01 (1H, ddd, J=8.0, 5.2, 2.4 Hz, H_1), 3.46 (1H, m, H_2), 3.45 (1H, br s, OH), 3.33 (1H, m, H_3), 1.8–1.2 (6H, m). Further elution gave the epoxide (**48**) (4 mg, 2%).

4.3.12. *cis*-2,3-Epoxy-3,5,5-trimethylcyclohexan-1-ol (54). This compound was prepared by the method of Magnusson[34] from isophorol (140 mg, 1 mmol) and gave the epoxide (**54**) (154 mg, 99%) as a colourless oil; ν_{max} (film) 3300, 1040 cm^{-1}; δ_H 4.00 (1H, ddd, J=11.1, 6.1, 2.0 Hz, H_1), 3.08 (1H, d, J=2.1 Hz, H_2), 1.57 (1H, d. J=15.0 Hz, H_{4a}), 1.37 (1H, ddd, J=12.1, 2.2, 6.1 Hz, H_{6a}), 1.38 (1H, br s, OH), 1.35 (1H, dd J=2.1, 15.0 Hz, H_{4b}),1.27 (3H, s, Me), 1.13 (1H, dd, J=12.1, 11.1 Hz, H_{6b}), 0.82 (3H, s, Me). 0.78 (3H, s, Me); δ_C 65.4 (C_1), 62.2 (C_2), 61.0 (C_3), 42.2 (C_4), 39.8 (C_6), 31.2 (C_5), 31.1 (Me), 26.3 (Me), 24.6 (Me).

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