A New Route to Epoxides and Ketones by *m*-Chloroperbenzoic Acid Oxidation of β-Hydroxyalkyl Phenyl Selenides and Tellurides

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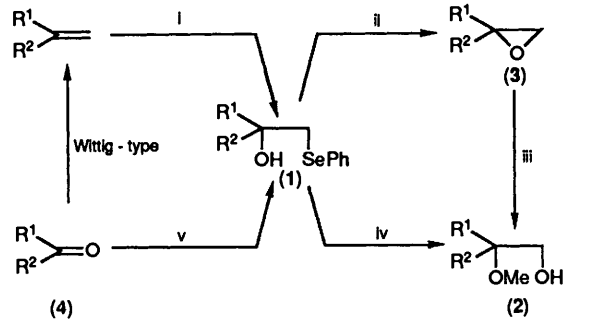
Treatment of primary (β-hydroxy)alkyl phenyl selenides [$R^1R^2C(OH)CH_2SePh$] with *m*- chloroperbenzoic acid (3–5 mol equiv.) in tetrahydrofuran or methanol gives the corresponding epoxides in high yield. *cis*-1-Methylene-4-t-butylcyclohexane oxide is obtained stereospecifically from 4-t-butyl-1-(phenylselenomethyl)cyclohexanol prepared by the addition of α-(phenylseleno)-methyl anion to 4-t-butylcyclohexanone. On the other hand, similar oxidation of secondary (β-hydroxy)alkyl phenyl selenides [$R^1R^2C(SePh)CH_2OH$] affords the unexpected carboxylic acids or their esters. When a phenyl group is present on the carbon bearing the OH moiety in β-hydroxy selenides and tellurides [*i.e.*, $PhRC(OH)CH_2MPh$; M = Se, Te; R = alkyl], the oxidation is accompanied by phenyl migration to afford ketones. The reaction can be applied to one-carbon-homologated ring expansion of the benzene-ring-fused cyclic ketones by combining with the addition of an α-(phenylseleno)methyl or α-(phenyltelluro)methyl moiety to the ketones.

In sharp contrast to the well known selenoxide elimination leading to alkenes, treatment of alkyl phenyl selenides (RSePh) with an excess of *m*-chloroperbenzoic acid (MCPBA; 2–5 mol equiv.) in alcohols at room temperature affords the corresponding dialkyl ethers by substitution of a phenylselenium (PhSe) moiety with an alkoxy group.[1] Similar reactions proceed with alkyl phenyl tellurides (RTePh) as well.[1] We now report that the application of this reaction to various types of β-hydroxyalkyl phenyl selenide and telluride (herein abbreviated as β-hydroxy selenides and β-hydroxy tellurides respectively), particularly the selenides, leads to a selective and readily occurring formation of epoxides, ketones, ethers, or acids, the types of product depending strongly on the structure of the starting selenide or telluride. Combination of the present methodology with the preparative method for β-hydroxy selenides and β-hydroxy tellurides by the addition of α-(phenylseleno)methyl and α-(phenyltelluro)methyl anions to aldehydes or ketones allowed the preparation of one-carbon-homologated epoxides and ketones. Krief and co-workers have reported several preparative methods for epoxides[2a,b] and ketones[2c–e] from β-hydroxy selenides: conversion of the selenides into the selenonium salts followed by treatment with a strong alkali for obtaining epoxides,[2a] and treatment of the selenides with dichlorocarbene for obtaining either epoxides[2b] or ketones.[2c–e] Our procedure appears to be much more easy and convenient in some cases, and to be complementary to Krief's methods. The details of our findings are presented here.[3]

Results and Discussion

Synthesis of Epoxides, Acids, Ethers, and Ketones.—Treatment of 2-ethyl-2-hydroxypentadecyl phenyl selenide (**1a**), prepared by regiospecific hydroxyselenenylation[4] of 2-ethylpentadec-1-ene, with MCPBA (5 mol equiv.) in methanol at 25 °C for 20 h gave 1-hydroxy-2-ethyl-2-methoxypentadecane (**2a**) in 80% isolated yields (Scheme 1). In contrast, when the reaction was stopped after 0.5 h, 2-ethyl-2-tridecyloxirane (**3a**) was obtained as the sole product almost quantitatively. From experiments with different reaction times it was found that the oxirane (**3a**) is slowly converted into the glycol ether (**2a**) under the present reaction conditions. Several other β-hydroxy selenides were then prepared more generally by the reaction of a ketone or an aldehyde (**4**) with α-(phenylseleno)methyl-lithium[5] and were



a; $R^1 = C_{13}H_{27}$, R^2 = Et **d**; $R^1 = R^2 = [CH_2]_6$
b; $R^1 = C_{12}H_{25}$, R^2 = Me **e**; $R^1 = R^2 = (CH_2)_2CHBu^t(CH_2)_2$
c; $R^1 = C_8H_{17}$, R^2 = H **f**; $R^1 = R^2 = [CH_2]_{11}$

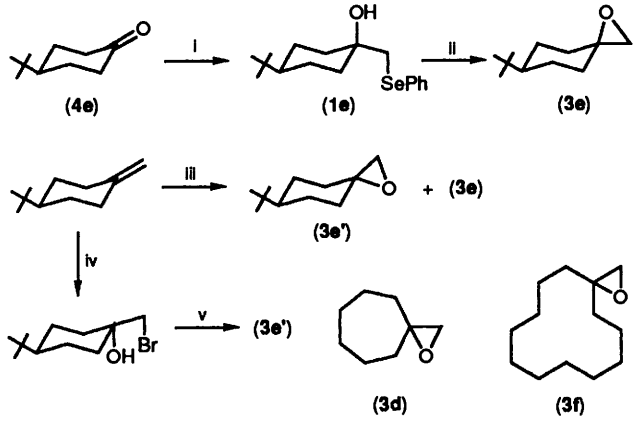
Scheme 1. *Reagents and conditions:* i, PhSeCl, aq. MeCN; ii, MCPBA (5 mol equiv.), MeOH or THF, 25 °C, 0.5–1 h; iii, MeOH; iv, MCPBA (5 mol equiv.), MeOH, 25 °C, 20 h; v, $PhSeCH_2Li$; then water.

then subjected to MCPBA oxidation in methanol. The products were mainly the corresponding epoxides which are one-carbon-homologated compounds of the starting ketones or aldehydes. Variable amounts of a ketone and/or a diol monomethyl ether, however, were also formed as side-products, and further work revealed that the use of tetrahydrofuran (THF) as solvent avoided the formation of such by-products. Typical results are shown in Table 1. It is worth noting that the one-carbon-homologated epoxide obtained from 4-t-butylcyclohexanone (**4e**) was only the *cis*-isomer (**3e**); none of the corresponding *trans*-isomer (**3e'**), prepared separately by a literature method[6] by the reaction of 4-t-butyl-1-methylenecyclohexane with *N*-bromoacetamide (NBA) followed by alkaline dehydrobromination, was detected by GLC analysis. This fact indicates that a hydroxy group of the starting β-hydroxyselenide (**1e**) stereospecifically occupies an axial position (Scheme 2). The selective formation of isomer (**3e**) by the reaction of ketone (**4e**) with dimethyloxosulphonium methylide is known.[7] For comparison the oxidation of the alkene with MCPBA was carried out in ethyl acetate to give a mixture of compounds (**3e**) and (**3e'**) [(**3e**):(**3e'**) 66:34 by GLC] in good yield. All these transformations are shown in Scheme 2, together with the structure of spiro-oxiranes (**3d**) and (**3f**) for convenience.

Table 1. Synthesis of β-hydroxy selenides (**1**) and their oxidation to epoxides (**3**).

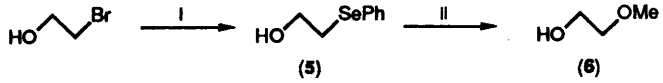
Aldehyde or ketone	β-Hydroxy selenide and yield/(%)[a]		Conditions for oxidation[b] Time (h)	Solvent	Product and yield (%)[c]	
(**4a**)	(**1a**)	73	0.5	MEOH	(**3a**)	96
(**4a**)	(**1a**)		20	MeOH	(**2a**)	80
(**4a**)	(**1a**)		2	THF	(**3a**)	72
(**4b**)	(**1b**)	69	0.5	THF	(**3b**)	73
(**4c**)	(**1c**)	74	1	MeOH	(**3c**)	31[d,e]
					(**2c**)	56[f]
(**4c**)	(**1c**)		1	THF	(**3c**)	73[d,g]
(**4d**)	(**1d**)	68	0.5	THF	(**3d**)	52[d]
(**4e**)	(**1e**)	66	1	MeOH	(**3e**)	66[d,h,i]
(**4e**)	(**1e**)		0.5	THF	(**3e**)	78[d,h]
(**4f**)	(**1f**)	69	0.5	MeOH	(**3f**)	100

[a] Isolated yield based on the initial amount of compound (**4**) employed. [b] The reaction was carried out with the selenide (**1**) (1 mmol) and MCPBA (5 mmol) in the solvent (10 ml) at 25 °C. [c] Isolated yield based on the initial amount of (**1**) employed. [d] GLC yield based on the initial amount of (**1**) employed. [e] Other product: decan-2-one (12%). [f] Regioisomeric mixture (GLC). [g] Other product: decan-2-one (8%). [h] Only *cis*-isomer. [i] Other products: compound (**2e**) and its regioisomer (34%).



Scheme 2. *Reagents and conditions:* i, $PhSeCH_2Li$; ii, MCPBA (5 mol equiv.), MeOH or THF, 25 °C; iii, MCPBA; iv, NBA; v, OH^-.

The easily accessible selenide (**1**) is a primary alkyl selenide bearing a secondary or tertiary hydroxy group at the β-position. In order to ascertain the scope and limitations of this oxidation, similar reactions were carried out using various types of β-hydroxy selenide such as compounds (**5**) (a primary alkyl selenide having a primary OH group), (**7**) (a secondary alkyl selenide having a primary OH group), (**10**) (a secondary alkyl selenide having a secondary OH group), and (**11**). As a result it was found that the expected epoxide was not the main product in all cases, and furthermore it was not obtained at all from the primary hydroxy compounds (**5**) and (**7**). Thus, the oxidation of 2-hydroxyethyl phenyl selenide (**5**) in methanol gave only the ethylene glycol monomethyl ether (**6**), irrespective of the reaction time and temperature, none of the ethylene oxide or the acetaldehyde being detected in the reaction products (Scheme 3). In the case of compound (**7**) the product was unexpectedly a



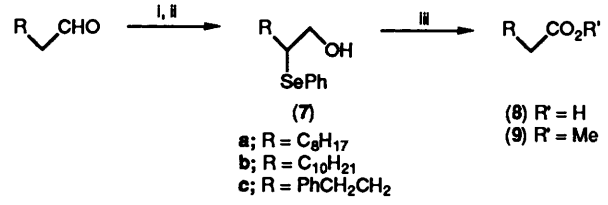
Scheme 3. *Reagents and conditions:* i, $PhSe^-$; ii, MCPBA (5 mol equiv.), MeOH, 25 °C or reflux.

carboxylic acid (**8**) or its methyl ester (**9**) when the reaction was performed in THF at 25 °C or in methanol at reflux temperature, respectively (Scheme 4). When the oxidation of 2-(phenylseleno)decan-1-ol (**7a**) was carried out in methanol at room temperature for 1 h, the products were decanal (18%) and a regioisomeric mixture of decane-1,2-diol monomethyl ethers (43%). The presence of decanal suggested that the oxidation shown in Scheme 4 proceeds *via* an aldehyde which is further oxidized to a carboxylic acid or its ester. Under any conditions employed for the oxidation of compounds (**7**) the formation of the expected epoxide was not observed. Typical results of the oxidation of compounds (**5**) and (**7**) are summarized in Table 2. It is interesting to note that oxidation of compound (**7a**) with H_2O_2 (2 mol equiv.) in THF at room temperature for 2 h gave only dec-2-en-1-ol, in 45% isolated yield, by the well known selenoxide elimination.

Table 2. MCPBA oxidation of β-hydroxy selenides (**5**) and (**7**)[a].

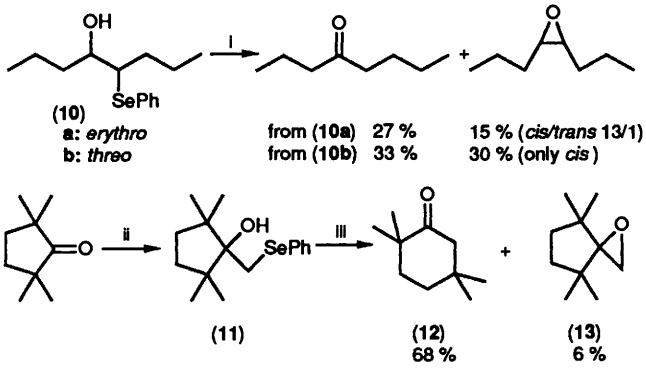
Selenide	Solvent	Temp (°C)	Time (h)	Product and yield (%)[b]	
(**5**)	MeOH	25	1	(**6**)	22
(**5**)	MeOH	25	5	(**6**)	34
(**5**)	MeOH	70	5	(**6**)	59
(**7a**)	THF	25	20	(**8a**)	39
(**7a**)	MeOH	70	5	(**9a**)	50
(**7b**)	THF	25	20	(**8b**)	30
(**7b**)	MeOH	70	5	(**9b**)	32
(**7c**)	THF	25	20	(**8c**)	30
(**7c**)	MeOH	70	5	(**9c**)	56

[a] The reaction was carried out with selenide (1 mmol) and MCPBA (5 mmol) in solvent (10 ml). [b] GLC yield based on the initial amount of selenide employed. The yield of the acid (**8**) was determined after esterification with diazomethane.



Scheme 4. *Reagents and conditions:* i, PhSeCl; ii, $LiAlH_4$; iii, MCPBA (5 mol equiv.), MeOH, reflux (or THF, 25 °C).

Oxidation of the selenides (**10**) and (**11**) proceeded rapidly to give the corresponding epoxides, but the main product was a ketone as shown in Scheme 5. Although compound (**11**) is a

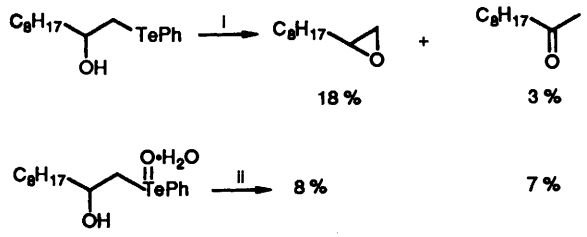


Scheme 5. *Reagents and conditions:* i, MCPBA (5 mol equiv.), MeOH, 25 °C; 30 min; ii, $PhSeCH_2Li$; iii, as for i, but 15 min only.

primary alkyl selenide bearing a tertiary OH group like compounds (**1a**), (**1b**), and (**1d–f**) the ring-expanded ketone (**12**) was obtained as the major product.

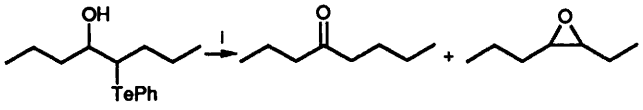
In contrast to the readily occurring oxidation of β-hydroxy selenides shown above, the oxidation of the corresponding β-hydroxy tellurides did not give the epoxides satisfactorily. Thus,

from 2-hydroxydecyl phenyl telluride the epoxide was obtained in only 18% yield after 24 h and no improvement was observed even with the corresponding telluroxide (Scheme 6, GLC yield).



Scheme 6. *Reagents and conditions:* i, MCPBA (5 mol equiv.), THF, 25 °C, 24 h; ii, as for i, but for 1 h only.

The tellurium analogues of compounds (**10**), namely *erythro*- and *threo*-5-hydroxy-4-octyl phenyl tellurides (**14a**) and (**14b**), respectively, gave the oxidation products in better yields than in the case of compounds (**10**), but the selectivity for the epoxides was low (Scheme 7; GLC yield). The stereospecific formation of



(**14**)

a: *erythro*	from (**14a**)	77%	9% (*cis*/*trans* 8/1)
b: *threo*	from (**14b**)	23%	48% (only *cis*)

Scheme 7. *Reagents and conditions:* i, MCPBA (5 mol equiv.), MeOH, 25 °C, 30 min.

a *cis*-epoxide* from the *threo*-hydroxy selenide and telluride (**10b**) and (**14b**) can be readily explained by an internal hydroxy-group participation, but the reason for the predominant formation of a *cis*-epoxide from the corresponding *erythro* compounds (**10a**) and (**14a**) is not clear.

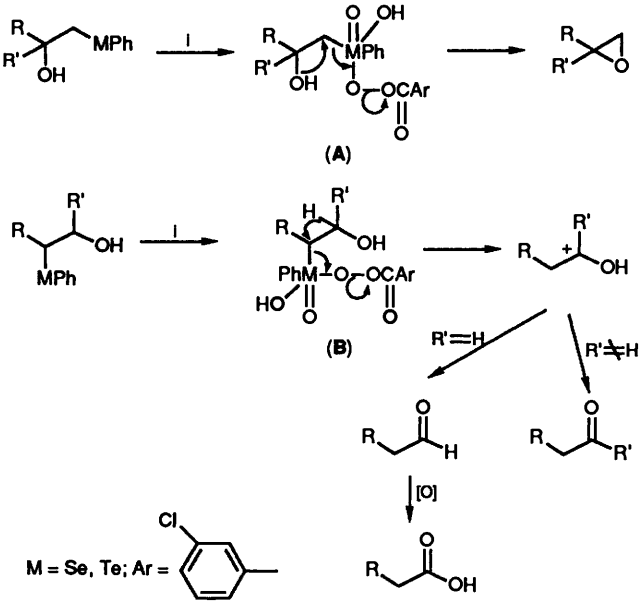
Taking account of the proposed scheme for substitution of PhSe and PhTe moieties by an alkoxy group in the treatment with an excess of MCPBA,[1] a general scheme for this oxidation may be postulated as shown in Scheme 8. An oxidized PhM moiety [PhM(O)(OH)(O$_2$COAr)] in the intermediate (**A**)† is a very good leaving group and intramolecular attack of oxygen gives an epoxide. On the other hand, in the case of secondary alkyl phenyl selenides such as compounds (**7**), (**10**), and (**14**), a hydride transfer may sometimes prevail over an intramolecular oxygen attack in a similar intermediate (**B**) to give a carbenium ion, which then loses a proton to give an aldehyde or a ketone. In the oxidation of compound (**11**) alkyl-group transfer prevails over intramolecular oxygen attack to result in ring expansion. Four methyl groups located vicinally to the hydroxy group may accelerate the expansion both electronically and stereochemically.

Synthesis of Ketones Accompanied by Phenyl Migration.— When the oxidation was applied to β-hydroxy selenides and β-hydroxy tellurides bearing a phenyl moiety at the carbon to which a hydroxy group is attached, phenyl migration occurred to afford only a ketone. Thus, addition of an α-(phenylseleno)-methyl[5] or α-(phenyltelluro)methyl moiety[8] to aryl ketones (**15**) such as acetophenone, benzophenone, and benzyl phenyl ketone followed by MCPBA treatment of the produced selenides or tellurides resulted in the formation of one-carbon-homologated aryl ketones (**16**) in fair yields (Scheme 9; Table 3).

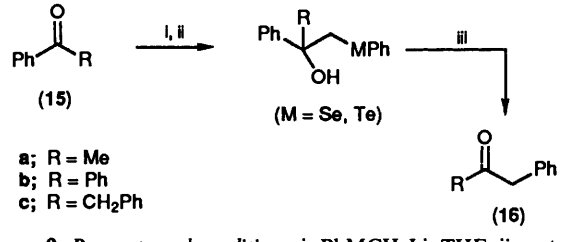
Table 3. One-carbon homologation of aryl ketones.

Ketone	$PhMCH_2^-$ addition step[a] M	Temp (°C)/Time (h)		Oxidation step[b] Temp (°C)/ Time (h)	Product and yield (%)[c]	
(**15a**)	Se	−78/2	25/12	25/1	(**16a**)	67
(**15b**)	Se	−78/2	25/2	25/1	(**16b**)	50[d]
(**15c**)	Se	−78/2	25/3	25/1	(**16c**)	83
(**15a**)	Te	−78/2	25/3	25/1	(**16a**)	26
(**15b**)	Te	−78/2	25/1	25/1	(**16b**)	30
(**15b**)	Te[e]	−78/2	25/4	25/1	(**16b**)	61

[a] Ketone (1 mmol), $(PhM)_2CH_2$ (1 mmol), and BuLi (1 mmol) were used. The mixture in THF (10 ml) was stirred at −78 °C for 2 h and then at 25 °C for 1–12 h. [b] The oxidation was carried out with MCPBA (5 mmol) in MeOH (10 ml). [c] GLC yield based on the initial amount of ketone (**15**) employed. [d] Isolated yield. [e] HMPA (2 mmol) was added.



Scheme 8. *Reagent:* i, MCPBA (excess).



Scheme 9. *Reagents and conditions:* i, $PhMCH_2Li$, THF; ii, water; iii, MCPBA (5 mol equiv.), MeOH, 25 °C, 1 h.

This oxidation was then applied to several benzene-ring-fused ketones (**17**) in the hope of achieving one-carbon-homologated ring expansion. Thus, addition of α-(phenylseleno)methyl anion to indan-1-one (**17a**), 1-tetralone (**17b**), 6-methoxy-1-tetralone (**17c**), 1-benzosuberone (**17d**), chroman-4-one (**17e**), and thiochroman-4-one (**17f**) afforded the corresponding β-hydroxy selenides (**18**) in fair to good yield. Oxidation of alcohols (**18**) with MCPBA (3 mol equiv.) in methanol readily gave the

* None of the corresponding *trans*-epoxide was detected by GLC analysis.

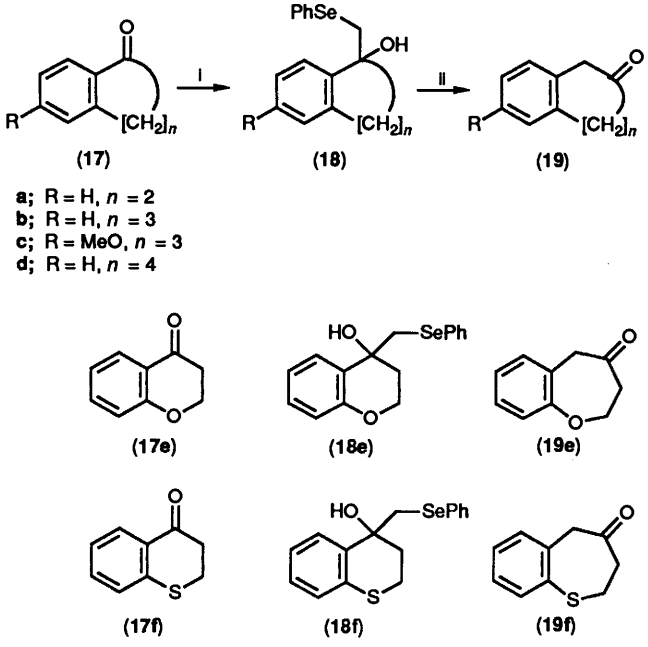
† Although we have not yet succeeded in isolating an adduct such as (**A**) or (**B**), we have recently isolated an MCBA-alkyl phenyl telluroxide adduct [RTe(OH)(OCOAr)Ph] as a white solid [R = cyclohexyl, m.p. 166–169 °C decomp.)] from the reaction of cyclohexyl phenyl telluride with MCPBA. Details will be reported elsewhere.

Table 4. Ring-expansion of benzene-ring-fused ketones.

Ketone (17)	β-Hydroxy selenide and yield (%)[a]	Conditions for oxidation Temp (°C)/Time (h)[b]	Product and yield (%)[c]
(17a)	(18a) 48	25/1.5	(19a) 74
(17b)	(18b) 61	25/0.5	(19b) 84
(17c)	(18c) 68	25/0.5	(19c) 70
(17d)	(18d) 77	25/0.5	(19d) 97
(17e)	(18e) 50	25/0.5	(19e) 51
(17f)	(18f) 55	25/0.5	*d*

[a] Isolated yield based on the initial amount of ketone (**17**) employed. [b] The oxidation was carried out with selenide (**18**) (1 mmol) and MCPBA (3 mmol) in methanol (10 ml). [c] Isolated yield based on the initial amount of β-hydroxy selenide (**18**) employed. [d] Only $(PhSe)_2$ was obtained.

expected ring-expanded ketones (**19**) in high yield, except in the case of compound (**18f**),* by aryl-group migration to the carbon bearing the PhSe moiety (Scheme 10; Table 4).



Scheme 10. *Reagents and conditions:* i, $PhSeCH_2Li$, THF; MCPBA (3 mol equiv.), MeOH, 25 °C, 30–90 min.

Experimental

^1H NMR spectra were recorded on Hitachi Perkin-Elmer R-600 (60 MHz), JEOL JNM-100 (100 MHz), and Varian VXR 200 (200 MHz) spectrometers for solutions in $CDCl_3$. ^{13}C NMR spectra were determined on a Fourier transform NMR system (JNM FX-100) for solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference Me_4Si. IR spectra were recorded on a Perkin-Elmer 521 or a JASCO IR-810 infrared spectrophotometer from thin films (for liquids). Mass spectra were measured on a JMS-DX 300 mass spectrometer, equipped with a JMA-3500 data processing system. M.p.s were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. GLC analyses [5% Silicone DC QF-1 (1 m), 25% PEG 6000 (1 and 3 m), and 3% EGSS-X (1 m) column on Chromosorb W 60–80 mesh] were performed on a Yanaco G 2800 instrument with flame-ionization detectors and N_2 as carrier gas. Column chromatography was performed with Wakogel C-200 (100–200 mesh). For preparative chromatography, plates precoated with Merck silica gel 60 F_{254} of 2 mm thickness were used.

Solvents were freshly distilled prior to use: methanol was distilled from magnesium methoxide prepared *in situ* from magnesium, iodine, and methanol; THF was distilled from benzophenone ketyl. Diphenyl ditelluride was prepared by the reported method.[9] The following known organic products such as compounds (**3c**),[10] (**3d**),[10,11] (**3e**),[7,11] (**3e'**),[6,11] octan-4-one,[12] and *cis*- and *trans*-oct-4-ene oxide[10] were prepared by the reported methods and were used as authentic samples or starting materials. 2-Ethylpentadec-1-ene was prepared in 77% isolated yield by treatment of hexadecan-3-one (**4a**) with CH_2Br_2, Zn, and $TiCl_4$ in THF at room temperature for 13 h;[13] δ_H (200 MHz) 0.88 (3 H, t), 1.02 (3 H, t), 1.20–1.40 (22 H, m), 1.94–2.08 (4 H, m), and 4.68 (2 H, s). All other commercial products were used without further purification.

The following β-hydroxyalkyl phenyl selenides and tellurides were prepared by reported methods.

2-(Phenylseleno)ethanol (**5**) was prepared in 94% yield from 2-bromoethanol, diphenyl diselenide, and $NaBH_4$;[14] δ_H (100 MHz) 2.50 (1 H, br m), 3.05 (2 H, t, *J* 6 Hz), 3.72 (2 H, br m), 7.15–7.40 (3 H, m), and 7.40–7.65 (2 H, m).

2-(*Phenylseleno*)*alkan*-1-*ols* (**7a–c**) were prepared by phenylselenenylation[15] of the aldehyde followed by $LiAlH_4$ reduction[16] in *ca.* 70% overall yield as pale yellow liquids.

Compound (**7a**); δ_H (100 MHz) 0.82–0.93 (3 H, m), 1.26–1.80 (14 H, m), 2.04 (1 H, br s), 3.16–3.41 (1 H, m), 3.50 (1 H, dd, *J* 12 and 6 Hz), 3.65 (1 H, dd, *J* 12 and 6 Hz), 7.20–7.38 (3 H, m), and 7.50–7.65 (2 H, m); δ_C (25.1 MHz) 14.2 (q), 22.7 (t), 27.8 (t), 29.3 (t), 29.4 (t), 31.8 (t), 31.9 (t), 50.4 (d), 64.4 (t), 127.7 (s), 127.8 (d), 129.1 (d), and 135.4 (d) (Found: M^+, 312.1131 and 314.1179. $C_{16}H_{26}OSe$ requires *M*, 312.1157 and 314.1149).

Compound (**7b**); δ_H (200 MHz) 0.88 (3 H, t), 1.16–1.65 (18 H, m), 2.25 (1 H, br s), 3.17–3.29 (1 H, m), 3.52 (1 H, dd, *J* 11.5 and 6.7 Hz), 3.63 (1 H, dd, *J* 11.5 and 5.0 Hz), 7.24–7.31 (3 H, m), and 7.54–7.59 (2 H, m); δ_C (25.1 MHz) 14.1 (q), 22.7 (t), 27.8 (t), 29.4 (t), 29.5 (t), 29.6 (t), 31.7 (t), 31.9 (t), 50.6 (d), 64.3 (t), 127.5 (s), 127.9 (d), 129.1 (d), and 135.4 (d) (Found: M^+, 340.1453 and 342.1477. $C_{18}H_{30}OSe$ requires *M*, 340.1470 and 342.1462).

Compound (**7c**); δ_H (200 MHz) 1.75–2.07 (2 H, m), 2.38 (1 H, br s), 2.69–2.99 (2 H, m), 3.11–3.24 (1 H, m), 3.55–3.58 (2 H, m), 7.12–7.32 (8 H, m), and 7.51–7.57 (2 H, m); δ_C (25.1 MHz) 33.2 (t), 33.9 (t), 49.5 (d), 64.5 (t), 126.1 (d), 127.3 (s), 128.1 (d), 128.49 (d), 128.52 (d), 129.2 (d), 135.5 (d), and 141.3 (s) (Found: M^+, 304.0567 and 306.0550. $C_{16}H_{18}OSe$ requires *M*, 304.0531 and 306.0523).

The selenides (**10**)[4] were prepared by oxyselenenylation of (Z)- and (E)-oct-4-ene, while the tellurides (**14**)[17] and 2-hydroxydecyl phenyl telluride[18] were prepared by ring-opening of the corresponding epoxides in > 90% yield.

Compound (**10a**); δ_H(200 MHz) 0.88 (3 H, t, *J* 6.6 Hz), 0.91 (3 H, t, *J* 6.6 Hz), 1.29–1.73 (8 H, m), 2.39 (1 H, d, *J* 6.2 Hz), 3.30 (1 H, m), 3.64 (1 H, m), 7.20–7.30 (3 H, m), and 7.50–7.62 (2 H, m); δ_C(25.1 MHz) 13.9 (q), 14.0 (q), 19.4 (t), 21.7 (t), 32.6 (t), 35.8 (t), 56.2 (d), 72.6 (d), 127.5 (d), 129.1 (d), 129.6 (d), and 134.4 (d) (Found: C, 58.9; H, 7.6. Calc. for $C_{14}H_{22}OSe$: C, 58.9; H, 7.8%).

Compound (**10b**); δ_H(200 MHz) 0.88 (3 H, t, *J* 7.2 Hz), 0.91 (3 H, t, *J* 6.8 Hz), 1.24–1.76 (8 H, m), 2.40 (1 H, br s), 3.11 (1 H, m), 3.56 (1 H, m), 7.20–7.29 (3 H, m), and 7.54–7.59 (2 H, m) (Found: M^+, 284.0844 and 286.0815. Calc. for $C_{14}H_{22}OSe$: *M*, 284.0844 and 286.0836).

* In the oxidation of compound (**18f**) with MCPBA (3 mol equiv.) in methanol at 25 °C for 30 min diphenyl diselenide was obtained in high yield, but the expected ring-expanded ketone (**19f**) was not detected in the products (by GLC and ^1H NMR analysis).

Compound (**14a**); δ_H(200 MHz) 0.88 (6 H, t, *J* 7.0 Hz), 1.31–1.80 (8 H, m), 2.18 (1 H, d, *J* 6.6 Hz), 3.45 (1 H, ddd, *J* 3.4, 7.6, and 6.5 Hz), 3.54 (1 H, m), 7.14–7.32 (3 H, m), and 7.77–7.82 (2 H, m); δ_C(25.1 MHz) 13.8 (q), 14.0 (q), 19.4 (t), 23.3 (t), 34.7 (t), 37.4 (t), 45.5 (d), 74.3 (d), 111.6 (s), 128.0 (d), 129.2 (d), and 139.7 (d).

Compound (**14b**); δ_H(200 MHz) 0.87 (3 H, t, *J* 7.0 Hz), 0.88 (3 H, t, *J* 7.0 Hz), 1.20–1.83 (8 H, m), 2.04–2.09 (1 H, m), 3.28 (1 H, m), 3.45 (1 H, m), 7.14–7.32 (3 H, m), and 7.75–7.83 (2 H, m); δ_C(25.1 MHz) 13.7 (q), 14.0 (q), 19.2 (t), 23.0 (t), 37.2 (t), 39.1 (t), 44.9 (d), 74.3 (d), 111.3 (s), 127.9 (d), 129.1 (d), and 140.0 (d).

1-(Phenyltelluro)decan-2-ol; δ_H(200 MHz) 0.87 (3 H, t, *J* 6.4 Hz), 1.14–1.55 (14 H, m), 2.24 (1 H, m), 2.97 (1 H, dd, *J* 12.2 and 8 Hz), 3.15 (1 H, dd, *J* 12.2 and 4 Hz), 3.63–3.77 (1 H, m), 7.14–7.28 (3 H, m), and 7.72–7.77 (2 H, m); δ_C(25.1 MHz) 14.1 (q), 20.4 (t), 22.7 (t), 26.0 (t), 29.2 (t), 29.6 (t), 31.9 (t), 38.0 (t), 71.1 (d), 111.3 (s), 127.8 (d), 129.3 (d), and 138.5 (d) (Found: C, 53.1; H, 7.2. Calc. for $C_{16}H_{26}OTe$: C, 53.1; H, 7.2%).

Preparation of β-*Hydroxyalkyl Phenyl Selenides from Carbonyl Compounds and* $PhSeCH_2Li$.—A typical experimental procedure is as follows. To a solution of $(PhSe)_2CH_2$* (1.63 g, 5.0 mmol) in THF (10 ml) at −78 °C under nitrogen was slowly added a solution of BuLi in hexane (2.9 ml, 5.4 mmol) and the resulting solution was stirred at the same temperature for 1.5 h. A solution of hexadecan-3-one (**4a**) (1.20 g, 5.0 mmol) in THF (5 ml) was then added to the above solution at −78 °C and the resulting solution was stirred at the same temperature for 2 h, and then for another 2 h at room temperature, when the solvent was evaporated off to leave a yellow oil, which was treated with $LiAlH_4$ (0.19 g, 5.0 mmol) in Et_2O (20 ml) to reduce unchanged ketone (**4a**) to hexadecan-3-ol which could be easily separated from the desired compound. Then aqueous 5M-NaOH was added dropwise until the precipitate turned from grey to white and became granular. The precipitate was filtered off and washed with Et_2O (100 ml). The filtrate was washed with brine and dried over $MgSO_4$. Evaporation of Et_2O left a yellow liquid, which was subjected to column chromatography on SiO_2 (Wakogel C-200) [hexane–EtOAc (10:1) as eluant] to give pale yellow, oily 3-(*phenylselenomethyl*)*hexadecan*-3-*ol* (**1a**) (1.49 g, 73%); δ_H (100 MHz) 0.78–0.93 (6 H, m), 1.26–1.70 (26 H, m), 2.03 (1 H, s), 3.13 (2 H, s), 7.20–7.38 (3 H, m), and 7.49–7.62 (2 H, m) (Found: M^+, 410.2236 and 412.2227. $C_{23}H_{40}OSe$ requires *M*, 410.2252 and 412.2244). Compound (**1a**) was also prepared by hydroxyselenenylation[4] of 2-ethylpentadec-1-ene in 66% isolated yield.

Other β-hydroxyalkyl phenyl selenides were similarly prepared and isolated, and purified by column chromatography on SiO_2 (Wakogel C-200) [hexane–EtOAc (10:1) as eluant] as follows.

2-(*Phenylselenomethyl*)*tetradecan*-2-*ol* (**1b**): a pale yellow oil (1.32 g, 69%); δ_H(100 MHz) 0.82–0.94 (3 H, m), 1.05–1.60 (25 H, m), 2.12 (1 H, s), 3.14 (1 H, s), 7.16–7.30 (3 H, m), and 7.44–7.60 (2 H, m) (Found: M^+, 382.1945 and 384.1948. $C_{21}H_{36}OSe$ requires *M*, 382.1939 and 384.1931).

1-(*Phenylseleno*)*decan*-2-*ol* (**1c**): a pale yellow oil (1.16 g, 74%); δ_H(100 MHz) 0.81–0.93 (3 H, m), 1.25–1.69 (14 H, m), 2.42 (1 H, d, *J* 3.9 Hz), 2.86 (1 H, dd, *J* 12.8 and 8.3 Hz), 3.15 (1 H, dd, *J* 12.8 and 3.4 Hz), 3.58–3.74 (1 H, m), 7.19–7.30 (3 H, m), and 7.43–7.58 (2 H, m); δ_C(25.1 MHz) 14.1 (q), 22.7 (t), 25.9 (t), 29.3 (t), 29.6 (t), 31.9 (t), 36.7 (t), 37.3 (t), 69.9 (d), 127.2 (d), 129.2 (d), 129.5 (s), and 133.0 (d) (Found: C, 61.5; H, 8.4. $C_{16}H_{26}OSe$ requires C, 61.3; H, 8.4%).

* Bis(phenylseleno)methane and bis(phenyltelluro)methane were prepared by a diazomethane insertion reaction to the Se–Se and Te–Te bonds of diphenyl diselenide and diphenyl ditelluride, respectively.[9]

1-(*Phenylselenomethyl*)*cycloheptanol* (**1d**): a pale yellow liquid (0.963 g, 68%); δ_H(100 MHz) 1.55–1.72 (12 H, m), 2.19 (1 H, s), 3.16 (2 H, s), 7.19–7.28 (3 H, m), and 7.45–7.61 (2 H, m); δ_C(25.1 MHz) 22.6 (t), 29.5 (t), 41.0 (t), 44.8 (t), 74.8 (s), 126.9 (d), 128.1 (s), 129.1 (d), and 132.6 (d) (Found: M^+, 282.0700 and 284.0642. $C_{14}H_{20}OSe$ requires *M*, 282.0687 and 284.0679).

4-t-*Butyl*-1-(*phenylselenomethyl*)*cyclohexanol* (**1e**): a white solid (1.07 g, 66%), m.p. 60–62 °C; δ_H(100 MHz) 0.85 (9 H, s), 1.25–1.82 (9 H, m), 1.97 (1 H, s, OH), 3.08 (2 H, s), 7.19–7.29 (3 H, m), and 7.46–7.60 (2 H, m); δ_C(25.1 MHz) 22.7 (t), 27.6 (q), 32.4 (s), 37.7 (t), 44.9 (t), 47.8 (d), 70.3 (s), 126.8 (d), 127.8 (s), 129.1 (d), and 132.5 (d) (Found: C, 62.5; H, 7.65. $C_{17}H_{26}OSe$ requires C, 62.8; H, 8.05%).

1-(*Phenylselenomethyl*)*cyclododecanol* (**1f**): a white solid (1.23 g, 69%), m.p. 55–57 °C; δ_H(200 MHz) 1.12–1.75 (22 H, m), 2.10 (1 H, s), 3.11 (2 H, s), 7.19–7.30 (3 H, m), and 7.50–7.62 (2 H, m) (Found: C, 64.9; H, 9.0. $C_{19}H_{30}OSe$ requires C, 64.6; H, 8.6%).

2,2,5,5-Tetramethyl-1-(phenylselenomethyl)cyclopentanol (**11**): a pale yellow liquid (1.26 g, 74%); δ_H(100 MHz) 1.08 (12 H, s), 1.03–1.84 (4 H, m), 2.5 (1 H, s), 3.24 (2 H, s), 7.18–7.30 (3 H, m), and 7.47–7.62 (2 H, m).

1-(*Phenylselenomethyl*)*indan*-1-*ol* (**18a**): a yellow oil (0.72 g, 48%); δ_H(100 MHz) 1.94–2.45 (2 H, m), 2.57–3.04 (2 H, m), 2.73 (1 H, s), 3.27 (1 H, d, *J* 12.5 Hz), 3.40 (1 H, d, *J* 2.5 Hz), 7.05–7.39 (7 H, m), and 7.41–7.53 (2 H, m); δ_C(25.1 MHz) 29.4 (t), 40.4 (t), 40.5 (t), 82.9 (s), 122.8 (d), 125.0 (d), 126.7 (d), 126.9 (d), 128.5 (d), 129.1 (d), 130.9 (s), 132.6 (d), 142.9 (s), and 146.0 (s) (Found: C, 63.5; H, 5.4. $C_{16}H_{16}OSe$ requires C, 63.4; H, 5.3%).

1-(*Phenylselenomethyl*)-1,2,3,4-*tetrahydronaphthalen*-1-*ol* (**18b**): a pale brown oil (0.964 g, 61%); δ_H(100 MHz) 1.53–2.33 (4 H, m), 2.69 (1 H, s), 2.75 (2 H, t, *J* 5.9 Hz), 3.37 (1 H, d, *J* 12.5 Hz), 3.46 (1 H, d, *J* 12.5 Hz), 6.95–7.29 (6 H, m), and 7.38–7.59 (3 H, m); δ_C(25.1 MHz) 20.1 (t), 29.6 (t), 36.6 (t), 43.3 (t), 72.3 (s), 126.2 (d), 126.4 (d), 127.0 (d), 127.5 (d), 128.8 (d), 129.1 (d), 130.9 (s), 132.9 (d), 136.8 (s), and 140.7 (s) (Found: C, 64.6; H, 5.7. $C_{17}H_{18}OSe$ requires C, 64.35; H, 5.7%).

6-*Methoxy*-1-(*phenylselenomethyl*)-1,2,3,4-*tetrahydronaphalen*-1-*ol* (**18c**): a pale yellow oil (1.18 g, 68%); δ_H(200 MHz) 1.62–2.25 (4 H, m), 2.49 (1 H, s), 2.71–2.79 (2 H, m), 3.39 (1 H, d, *J* 12.6 Hz), 3.50 (1 H, d, *J* 12.6 Hz), 3.77 (3 H, s), 6.59 (1 H, d, *J* 2.5 Hz), 6.76 (1 H, dd, *J* 8.5 and 2.5 Hz), 7.20–7.28 (3 H, m), 7.48 (1 H, d, *J* 8.5 Hz), and 7.52–7.59 (2 H, m); δ_C(25.1 MHz) 20.2 (t), 30.1 (t), 36.7 (t), 43.3 (t), 55.2 (q), 72.1 (s), 112.7 (d), 113.2 (d), 127.0 (d), 127.7 (d), 129.2 (d), 131.0 (s), 132.8 (d), 138.5 (s), and 158.7 (s) (Found: M^+, 346.0639 and 348.0620. $C_{18}H_{20}O_2Se$ requires *M*, 346.0636 and 348.0629).

5-(*Phenylselenomethyl*)-6,7,8,9-*tetrahydro*-5H-*benzocycloheptene*-5-*ol* (**18d**): a pale yellow oil (1.28 g, 77%); δ_H(100 MHz) 1.51–2.12 (6 H, m), 2.80 (2 H, m), 2.88 (1 H, s), 3.51 (1 H, d, *J* 12.5 Hz), 3.56 (1 H, d, *J* 12.5 Hz), 6.82–7.28 (7 H, m), and 7.30–7.51 (2 H, m); δ_C(25.1 MHz) 26.0 (t), 27.7 (t), 37.0 (t), 40.5 (t), 41.5 (t), 76.5 (s), 126.0 (d), 126.3 (d), 127.0 (d), 127.4 (d), 129.0 (d), 130.5 (s), 130.9 (d), 133.0 (d), 139.4 (s), and 144.6 (s) (Found: C, 65.2; H, 6.2. $C_{18}H_{20}OSe$ requires C, 65.25; H, 6.1%).

4-(*Phenylselenomethyl*)*chroman*-4-*ol* (**18e**): a pale yellow oil (0.80 g, 50%); δ_H(200 MHz) 2.07 (1 H, ddd, *J* 14, 7.1, and 4 Hz), 2.24 (1 H, ddd, *J* 14, 7.7, and 3.6 Hz), 2.69 (1 H, br s, OH), 3.45 (1 H, d, *J* 12.8 Hz), 3.54 (1 H, d, *J* 12.8 Hz), 4.06 (1 H, ddd, *J* 11.3, 7.1, and 3.6 Hz), 4.18 (1 H, ddd, *J* 11.3, 7.7, and 4.0 Hz), 6.81 (1 H, d, *J* 8.2 Hz), 6.90 (1 H, dd, *J* 7.6 Hz), 7.17 (1 H, dd, *J* 8.2 Hz), 7.23–7.26 (3 H, m), 7.43 (1 H, d, *J* 7.8 Hz), and 7.52–7.57 (2 H, m); δ_C(25.1 MHz) 35.5 (t), 42.1 (t), 63.2 (t), 68.4 (s), 117.1 (d), 120.8 (d), 126.4 (d, s; overlapping), 127.2 (d), 129.2 (d), 129.5 (d), 130.5 (s), 132.9 (d), and 154.3 (s) (Found: C, 59.95; H, 5.0. $C_{16}H_{16}O_2Se$ requires C, 60.2; H, 5.05%).

4-(*Phenylselenomethyl*)*thiochroman*-4-*ol* (**18f**): a yellow oil (0.93 g, 55%); δ_H(100 MHz) 1.92–2.91 (4 H, m), 2.74 (1 H, s, OH), 3.29 (1 H, d, *J* 13.2 Hz), 3.45 (1 H, d, *J* 13.2 Hz), 6.98–7.10 (3 H,

m), 7.17–7.29 (3 H, m), and 7.44–7.65 (3 H, m); δ_C(25.1 MHz) 23.2 (t), 34.6 (t), 41.1 (t), 71.3 (s), 124.4 (d), 126.0 (d), 126.2 (d), 127.3 (d), 127.8 (d), 129.2 (d), 130.2 (s), 132.6 (s), 133.0 (d), and 137.9 (s) (Found: C, 57.8; H, 4.95. $C_{16}H_{16}OSSe$ requires C, 57.3; H, 4.8%).

Oxidation of β-Hydroxyalkyl Phenyl Selenides.—A general procedure is as follows. To a stirred solution of compound (**1a**) (0.412 g, 1.0 mmol) in MeOH (10 ml) at 25 °C was added 80% MCPBA (1.079 g, 5.0 mmol as pure MCPBA). The resulting solution was stirred for 0.5 h, treated with aqueous 1M-$Na_2S_2O_3$ (50 ml), and extracted with Et_2O (3 × 30 ml). The extract was washed with aqueous 0.5M-NaOH (50 ml) and dried over $MgSO_4$. Evaporation of the solvent left a yellow oil, which was subjected to column chromatography on SiO_2 with hexane–EtOAc (10:1) as eluant to afford *2-ethyl-2-tridecyloxirane* (**3a**) (0.244 g, 96%); δ_H(200 MHz) 0.75–1.05 (6 H, m), 1.12–1.18 (26 H, m), and 2.57 (2 H, s) (Found: C, 79.9; H, 13.4. $C_{17}H_{34}O$ requires C, 80.2; H, 13.5%).

By similar treatment of compound (**1a**) (1.0 mmol) for a longer time (20 h), *2-ethyl-2-methoxypentadacan-1-ol* (**2a**) was obtained as a liquid (0.230 g, 80%); δ_H(200 MHz) 0.77–0.92 (6 H, m), 1.26–1.54 (26 H, m), 1.84 (1 H, br s), 3.17 (3 H, s), and 3.45 (2 H, s); δ_C(25.1 MHz) 7.55 (q, t; overlapping), 14.1 (q, t; overlapping), 22.6 (t), 23.0 (t), 24.3 (t), 29.3 (t), 29.6 (t), 30.3 (t), 31.4 (t), 31.9 (t), 48.5 (q), 63.1 (t), and 79.1 (s) (Found: C, 75.0; H, 13.5. $C_{18}H_{38}O_2$ requires C, 75.5; H, 13.8%).

The following oxiranes were similarly prepared. *2-Dodecyl-2-methyloxirane* (**3b**): a liquid (0.165 g, 73%); δ_H(200 MHz) 0.84–0.92 (3 H, m), 1.22–1.55 (22 H, m), 1.29 (3 H, s), 2.56 (1 H, d, *J* 5.0 Hz), and 2.60 (1 H, d, *J* 5.0 Hz) (Found: M^+, 226.2301. $C_{15}H_{30}O$ requires *M*, 226.2297).

Methylenecyclododecane oxide (**3f**): a pale yellow liquid (0.195 g, 100%); δ_H(200 MHz) 1.27–1.73 (22 H, m), and 2.57 (2 H, s). (Found: M^+, 196.1826. $C_{13}H_{24}O$ requires *M*, 196.1827).

The yields of the known compounds (**3c**), (**3d**), and (**3e**) were determined by GLC analysis using a suitable internal standard.

Homologation of Aromatic Ketones via *(Phenylseleno)methylation or (Phenyltelluro)methylation followed by* MCPBA *Oxidation.*—A typical experimental procedure is as follows. To a solution of $(PhTe)_2CH_2$ * (0.425 g, 1.0 mmol) in THF (5 ml) at −78 °C was slowly added a solution of BuLi in hexane (17.4% w/w; 0.6 ml, 1.1 mmol) under nitrogen and the resulting solution was stirred at the same temperature for 1.5 h. Then a solution of benzophenone (**15b**) (0.18 g, 1.0 mmol) and hexamethylphosphoric triamide (HMPA) (0.36 g, 2.0 mmol) in THF (5 ml) was added to the above solution at −78 °C, the resulting solution was stirred at −78 °C for 2 h, and then for 4 h at room temperature, and the solvent was evaporated off to leave an orange oil, which was dissolved in MeOH (10 ml). To this solution at room temperature was added 80% MCPBA (1.078 g, 5.0 mmol as pure MCPBA). The mixture was stirred at room temperature for 1 h, treated with aqueous 1M-$Na_2S_2O_3$ (50 ml), and then extracted with Et_2O (3 × 30 ml). The extract was washed with aqueous 0.5M-NaOH (50 ml) to remove the produced *m*-chlorobenzoic acid and then the product, benzyl phenyl ketone (**16**; R = Ph), was determined by GLC with dibenzyl ketone as internal standard.

Ring-expansion Reaction of Alcohols (**18**) *with* MCPBA.—A general procedure is as follows. To a stirred solution of an alcohol (**18**) (1.0 mmol) in MeOH (10 ml) at 25 °C was added 80% MCPBA (0.65 g, 3.0 mmol as pure MCPBA). The resulting solution was stirred for 0.5 h, treated with aqueous 1M-$Na_2S_2O_3$ (50 ml), and extracted with Et_2O (3 × 30 ml). The extract was washed with aqueous 0.5M-NaOH (50 ml) and dried over $MgSO_4$. The products, the ring-expanded ketones, were isolated by preparative TLC (PLC) or column chromatography on SiO_2.

3,4-Dihydronaphthalen-2(1H)-one (**19a**): Isolated by PLC as a red liquid (0.108 g, 74%); δ_H(100 MHz) 2.47–2.61 (2 H, m), 3.06 (2 H, t, *J* 6.9 Hz), 3.57 (2 H, s), and 7.09–7.24 (4 H, m); δ_C(25.1 MHz) 28.5 (t), 38.2 (t), 45.1 (t), 127.0 (d), 127.7 (d), 128.3 (d), 133.4 (s), 136.8 (s), and 210.3 (s); ν_{max}(film) 1 715 cm^{-1} (C=O).

5,7,8,9-Tetrahydrobenzocyclohepten-6-one (**19b**): Isolated by PLC as a liquid (0.135 g, 84%); δ_H(200 MHz) 1.92–2.05 (2 H, m), 2.57 (2 H, dd, *J* 6.9 Hz), 2.95 (1 H, dd, *J* 8.4 and 4.2 Hz), 2.95 (1 H, dd, *J* 6.2 Hz), 3.72 (2 H, s), and 7.13 (4 H, s): ν_{max}(film) 1 705 cm^{-1} (C=O).

2-Methoxy-5,7,8,9-tetrahydrocyclohepten-6-one (**19c**): Isolated by PLC as a yellow liquid (0.135 g, 70%); δ_H(200 MHz) 1.90–2.03 (2 H, m), 2.54 (2 H, t, *J* 6.9 Hz), 2.91 (2 H, m), 3.64 (2 H, s), 3.78 (3 H, s), 6.67–6.72 (2 H, m), and 7.05 (1 H, d, *J* 8.0 Hz); ν_{max}(film) 1 705 cm^{-1} (C=O) (Found: C, 75.5; H, 7.4. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%).

7,8,9,10-*Tetrahydrobenzocyclo-octen-6(5H)-one* (**19d**): Isolated by PLC as a pale yellow liquid (0.169 g, 97%); δ_H(200 MHz) 1.58–1.91 (4 H, m), 2.29–2.35 (2 H, m), 2.78–2.83 (2 H, m), 3.78 (2 H, s), and 7.10–7.25 (4 H, m); ν_{max}(film) 1 700 cm^{-1} (C=O) (Found: C, 82.6; H, 8.15. $C_{12}H_{14}O$ requires C, 82.7; H, 8.1%).

2,3-*Dihydro*[1]*benzoxepin-4(5H)-one* (**19e**): Isolated by column chromatography, with hexane–EtOAc (5:1) as eluant, as a pale yellow liquid (0.082 g, 51%); δ_H(200 MHz) 2.85 (2 H, t, *J* 6.0 Hz), 3.84 (2 H, s), 4.38 (2 H, t, *J* 6.0 Hz), and 6.99–7.26 (4 H, m); ν_{max}(film) 1 720 cm^{-1} (C=O) (Found: M^+, 162.0691. $C_{10}H_{10}O_2$ requires *M*, 162.0681).

Oxidation of the Alcohol (**11**) *with* MCPBA.—To a stirred solution of the alcohol (**11**) (0.624 g, 2.0 mmol) in MeOH (20 ml) at 25 °C was added 80% MCPBA (2.157 g, 10 mmol as pure MCPBA). After the resulting solution had been stirred for 15 min, it was added to aqueous 1M-$Na_2S_2O_3$ (50 ml) and then extracted with Et_2O (3 × 50 ml). The extract was washed with aqueous 0.5M-NaOH (100 ml) and dried over $MgSO_4$. Evaporation of the solvent left a yellow oil, which was distilled (Kugelrohr) to give a liquid (0.229 g), b.p. 130–140 °C/19 mmHg. The ^1H NMR (60 MHz) spectrum of the product revealed the presence of the ketone (**12**) together with a small amount of the spiro-oxirane (**13**) [(**12**):(**13**) 85:15 by GLC]. The ^1H NMR (60 MHz) spectrum of compound (**12**) was identical with that of the reported compound,[19] δ_H 0.95 (6 H, s), 1.10 (6 H, s), 1.64 (4 H, s), and 2.21 (2 H, s); ν_{max}(film) 1 705 cm^{-1} (C=O).

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