# Oxidation of Alkyl Phenyl Selenides, Tellurides, and Telluroxides with *meta*-Chloroperbenzoic Acid for a Facile and Novel Transformation of C–Se and C–Te Bonds to C–O Bonds

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In sharp contrast to the well-known selenoxide elimination leading to olefins, the treatment of alkyl phenyl selenides (PhSeR) with an excess of *meta*-chloroperbenzoic acid (MCPBA; 2—5 equiv. to a selenide) in alcohol at room temperature affords the corresponding dialkyl ethers by the substitution of a phenylselenium (PhSe) moiety with an alkoxy group. A similar reaction proceeds by using alkyl phenyl tellurides (PhTeR) and telluroxides [PhTe(O)R], a facile substitution of PhTe or PhTe(O) moiety by an alkoxy group being observed. Methanol is the most appropriate solvent for these oxidations and alkyl methyl ethers are formed in excellent yields. The reaction is accompanied by phenyl migration when applied to some selenides, tellurides, and telluroxides having a phenyl group at a vicinal position to the PhSe, PhTe, or PhTe(O) moiety. Application to the methoxyselenation and methoxytelluration products of cyclohexene and cycloheptene results in a ring-contraction to afford the dimethyl acetals of cyclopentane- and cyclohexane-carbaldehyde, respectively. In case of an allylic phenyl selenide, a [2,3]sigmatropic rearrangement giving a rearranged allylic alcohol occurs in much preference to the substitution by the methoxy group. Other oxidizing agents than MCPBA such as $NaIO_4$, $H_2O_2$, t-BuOOH, and ozone are generally ineffective under similar conditions. It is proposed that the reaction mainly takes place as follows. Alkyl phenyl selenone, alkyl phenyl tellurone, or the MCPBA addition product to them is formed as a reactive intermediate in which an alkyl C–Se or alkyl C–Te bond fission occurs heterolytically by a nucleophilic attack of alcohol, sometimes accompanied by a 1,2-shift of the β-substituent, *i.e.*, phenyl migration and ring-contraction.

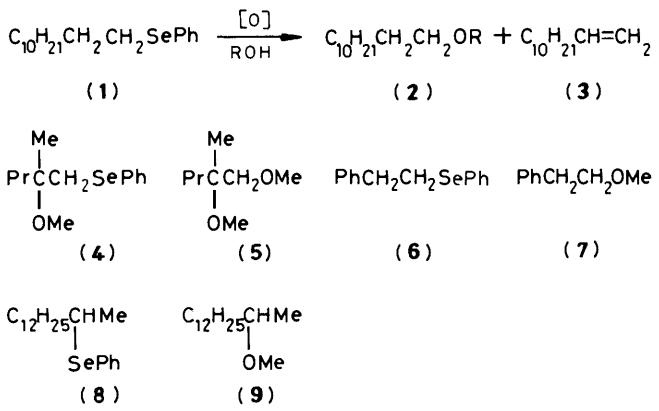
The selenoxide *syn* elimination is well-known as a double bond-forming reaction and has been widely used as a useful tool for organic synthesis.[1] In the reaction, an arylselenium moiety is introduced into compounds giving alkyl aryl selenides; oxidation of the latter with various oxidizing agents then leads to the corresponding selenoxides which readily eliminate arylselenenic acid (ArSeOH) when a β-hydrogen is present. In sharp contrast, we found that the oxidation of various alkyl phenyl selenides with an excess of *meta*-chloroperbenzoic acid (MCPBA) in alcohol solvents resulted in the replacement of a phenylselenium (PhSe) moiety by an alkoxy group to afford the corresponding alkyl ethers, aldehydes, or ketones instead of olefins. Although such reactions (C–Se→C–O) are known [*i.e.*, the formation of 1-dodecyl acetate from 1-dodecyl phenyl selenide and acidic $H_2O_2$,[2] oxetane ring formation from 1-alkyl-3-arylseleno-prop-2-en-1-ol,[3] and the formation of cinnamyl alcohol and cinnamyl ether by the oxidation of cinnamyl phenyl selenide with $H_2O_2$ in ethanol[4]] they are not widely known, and the parameters which control selection of these other pathways rather than elimination have been little examined.† Although similar transformations take place with alkyl phenyl tellurides and telluroxides, a phenyltellurium (PhTe) or phenyltelluronyl [PhTe(O)] moiety being substituted by an alkoxy group, the corresponding organosulphur compounds are completely unreactive under such conditions. In spite of both current and growing interest in the use of organotellurium compounds and inorganic tellurium salts in organic syntheses,[5,6] the few specific examples of the transformation of C–Te bonds into C–O bonds are a partial conversion of some alkyl phenyl tellurides into alcohols by the treatment with t-butyl hydroperoxide (Bu$^t$OOH)[2] and a conversion of benzyltellurium compounds into benzyl alcohol and/or benzaldehyde by the treatment with oxygen.[7] The results presented here have the potential of providing a general and facile method for transforming C–Se and C–Te bonds into C–O bonds.[8]

## Results and Discussion

*Alkyl Phenyl Selenides.*—Treatment of dodecyl phenyl selenide (**1**) with 1 equiv. of MCPBA in methanol at 25 °C for 1 h afforded dodec-1-ene (**3**) as expected together with a trace amount of dodecyl methyl ether (**2**; R = Me). In contrast, when 2—3 equiv. of MCPBA was used (**2**; R = Me) was obtained in over 80% yield together with a small amount of (**3**); use of 5 equiv. of MCPBA afforded (**2**; R = Me) alone and in almost quantitative yield. In no reaction was the formation of anisole, phenol, and dodecan-1-ol (**2**; R = H) observed. Methanol was shown to be the most appropriate solvent for the formation of (**2**), the reaction being slower in other alcohols even with 5 equiv. of MCPBA; the yield of the expected alkyl 1-dodecyl ether decreased in the following order: MeOH ≫ EtOH > Pr$^n$OH > Pr$^i$OH ≫ Bu$^t$OH (Scheme 1, Table 1). The formation of variable amounts of (**2**; R = H) was also observed in the oxidation in alcohols other than methanol.† Treatment of (**1**) with other oxidizing agents such as hydrogen peroxide, sodium periodate, t-butyl hydroperoxide, and ozone in methanol resulted in a selective elimination to give (**3**) even when an excess of reagent was used. It was also observed that in the presence of an acid such as trifluoroacetic acid or boron trifluoride–diethyl ether the oxidation of (**1**) with an excess of hydrogen peroxide afforded a considerable amount of (**2**; R = Me), although (**3**) was still the major product. These results clearly show that MCPBA is a specific oxidizing agent for the facile formation of

† Pummerer-like rearrangement of α-phenylselenoketones and β-ketoseleninic acids have been known to give α,α-dimethoxyketones or α-diketones: for example, H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, 1975, **97**, 5434; K. B. Sharpless and K. M. Gordon, *ibid.*, 1976, **98**, 300; Y. Nagao, M. Ochiai, K. Kaneko, A. Maeda, K. Watanabe, and E. Fujita, *Tetrahedron Lett.*, 1977, 1345.

† Although the details on the formation are not yet known (**2**; R = H) is presumably the result of 1,2-shift of either the corresponding selenoxide or selenone as proposed in the oxidation of some tellurides.[2]



Scheme 1.

**Table 1.** Oxidation of dodecyl phenyl selenide (**1**) leading to the ether (**2**) and the olefin (**3**)[a]

| Solvent (ROH) R | Reaction time (h) | Oxidizing agent | Equiv.[b] | Products and yields (%)[c] (2) | (3) |
|---|---|---|---|---|---|
| Me | 1 | MCPBA | 1 | Trace | 39 |
| Me | 1 | MCPBA | 2 | 80 | 5 |
| Me | 1 | MCPBA | 3 | 80 | 7 |
| Me | 1 | MCPBA | 5 | 97 | 0 |
| Et | 1 | MCPBA | 5 | 36[d] | 7 |
| Et | 24 | MCPBA | 5 | 45 | 7 |
| $Pr^n$ | 24 | MCPBA | 5 | 29[e] | 8 |
| $Pr^i$ | 24 | MCPBA | 5 | 11[f] | 10 |
| $Bu^t$ | 24 | MCPBA | 5 | 0[g] | 7 |
| $CH_2Cl_2$[h] | 1 | MCPBA | 2 | 0[i] | 57 |
| Me | 1 | $H_2O_2$ | 5 | 0[i] | 40 |
| Me | 24 | $H_2O_2$ | 5 | 0[i] | 66 |
| Me[j] | 24 | $H_2O_2$ | 5 | 24 | 60 |
| Me[k] | 24 | $H_2O_2$ | 5 | 34 | 52 |
| Me/H[l] | 1 | $NaIO_4$ | 5 | 0 | 47 |
| Me | 1 | $Bu^tO_2H$ | 5 | 0 | 38 |
| Me | 1 | $O_3$ | Excess | Trace | 70 |

[a] Compound (**1**) (1 mmol), solvent (10 ml), at 25 °C. [b] Mole equivalent to compound (**1**). [c] G.l.c. yield with an internal standard. [d] $C_{12}H_{25}OH$ [(**2**; R = H)] (14%). [e] $C_{12}H_{25}OH$ (10%). [f] $C_{12}H_{25}OH$ (20%). [g] $C_{12}H_{25}OH$ (28%). [h] Dichloromethane as the solvent. [i] $C_{12}H_{25}OH$ (<5%). [j] $CF_3CO_2H$ (5 mmol) was added. [k] $BF_3$·$Et_2O$ (5 mmol) was added. [l] 50% Aqueous MeOH.

(**2**) in preference to selenoxide elimination. It is worth noting that dodecyl phenyl sulphide [sulphur analogue of (**1**)] gave neither (**2**) nor (**3**) when similarly treated (3—5 equiv. of MCPBA at 25 °C for 1 h).*

Since the reaction system of 5 equiv. of MCPBA/MeOH at 25 °C for 1 h has been shown to be suitable for a ready and nearly quantitative replacement of PhSe by an alkoxy group, we applied this reaction system to various organic selenides (see Table 2). As shown in the Table, the use of 2 equiv. of MCPBA and a shorter reaction time (5—10 min) was also sometimes enough. The treatment of primary alkyl selenides (**4**) and (**6**) afforded, solely, (**5**) and (**7**) respectively, whilst the secondary alkyl selenide (**8**) gave mainly the corresponding methyl ether (**9**) together with small amounts of tetradec-1- and -2-enes.

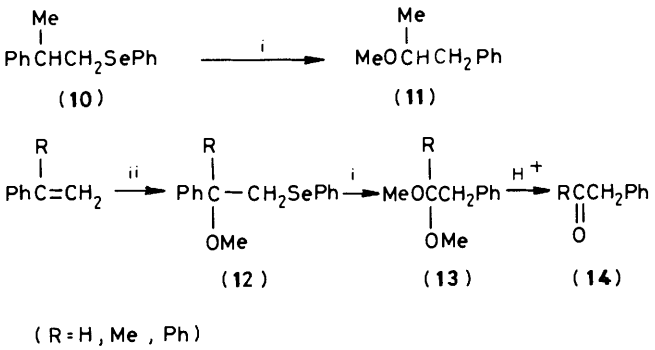
* Similarly, the treatment of phenyl 2-phenylpropyl sulphide [sulphur analogue of (**10**)] with 5 equiv. of MCPBA in methanol failed to undergo reaction even under reflux for 12 h, the sulphide being completely recovered after reduction with aqueous $Na_2S_2O_3$

**Table 2.** MCPBA Oxidation of various selenides in methanol[a]

| Selenides | Product | Yield (%)[b] |
|---|---|---|
| (**1**) | (**2**) | 97 |
| (**4**)[c] | (**5**) | 85[d] |
| (**6**) | (**7**) | 95,[d] Styrene trace |
| (**8**) | (**9**) | 90, Tetradec-1- and -2-enes 10 |
| (**10**) | (**11**) | 100 |
| (**12**; R = H) | (**13**) | 100 |
| (**12**; R = H)[e] | (**13**) | 93 |
| (**12**; R = H)[e,f] | (**13**) | 83 |
| (**12**; R = Me) | (**14**; R = Me) | 100 |
| (**12**; R = Ph) | (**14**; R = Ph) | 100 |
| (**15**) | (**16**) | 100 |
| (**15**)[e] | (**16**) | 85, (**18**) 15 |
| (**15**)[g] | (**17**) | 80, (**18**) 20 |
| (**15**)[h] | (**18**) | 100 |
| (**19**; R = H) | (**21**; R = H) | 100 |
| (**19**; R = Me) | (**21**; R = Me) | 100 |
| (**22**)[c] | (**23**) | 80[d] |
| (**24**)[c] | (**25**) | 90[d,i] |
| (**24**)[c,h] | (**26**) | 80[d] |
| (**27**)[c] | (**28**) | 70[d,j] |
| (**29**)[e] | (**30**) | 96 (90),[d] (**31**) 2, (**32**) 2 |
| (**29**)[k] | (**30**) | 62, (**31**) 2, (**32**) 2, Cinnamaldehyde 12 |

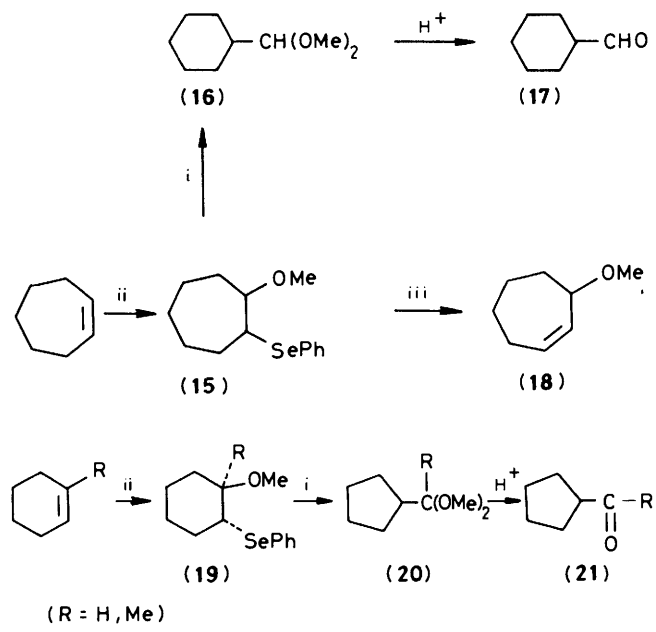
[a] Selenide (1 mmol), MCPBA (5 mmol), MeOH (10 ml), at 25 °C for 1 h. [b] G.l.c. yield with an internal standard. [c] Selenide (5 mmol), MCPBA (25 mmol), MeOH (30 ml). [d] Isolated yield. [e] Selenide (1 mmol), MCPBA (2 mmol), MeOH (10 ml). [f] For 10 min. [g] EtOH as the solvent. [h] Selenide (1 mmol), $H_2O_2$ (5 mmol), THF or MeOH (10 ml). [i] *cis*:*trans* = 58:42. [j] *cis*:*trans* = 40:60. An unidentifed compound, not the dimethyl acetal of a ring-contracted aldehyde, was also present (*ca.* 20%). [k] Selenide (1 mmol), MCPBA (1 mmol), MeOH (10 ml).

On the other hand, when (**10**) was treated under the same conditions, (**11**) was obtained quantitatively as the sole product, none of the expected unrearranged ether, methyl 2-phenylpropyl ether, being detected (see Scheme 2). This means that replacement of PhSe by a methoxy group was accompanied by phenyl migration. Similar phenyl migration was also observed in the cases of (**12**; R = H), (**12**; R = Me), and (**12**; R = Ph) (see Scheme 2 and Table 2).



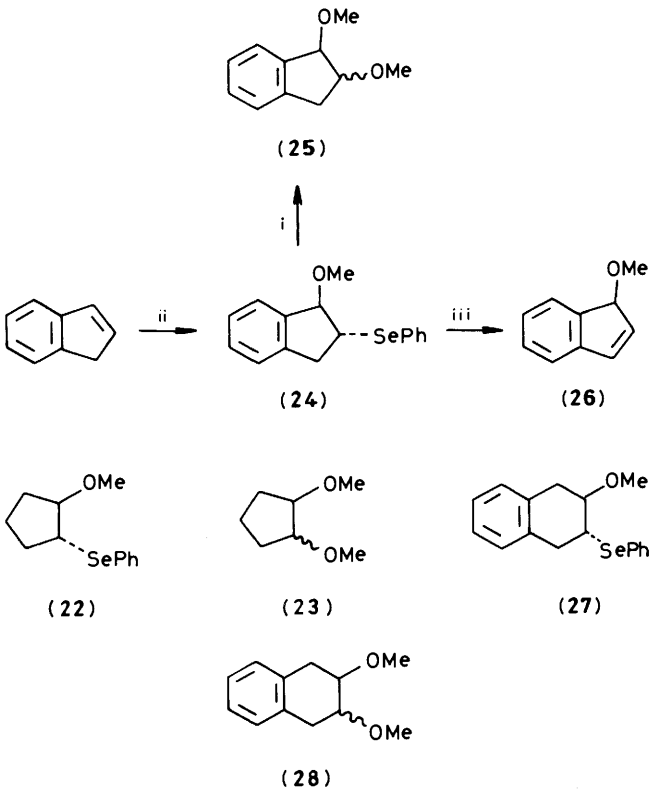
Scheme 2. *Reagents and conditions:* i, MCPBA–MeOH (25 °C for 1 h); ii, PhSeCl–MeOH–$Et_3N$ (25 °C for 2h)

Similarly, the methoxyselenation products of cyclic olefins such as (**15**) and (**19**) were oxidized readily and quantitatively to the dimethyl acetals of the ring-contracted cycloalkanecarbaldehydes (**16**) and (**20**) respectively, while a quantitative yield of the allylic ether (**18**) was obtained from (**15**) by use of 5 equiv. of $H_2O_2$ as the oxidizing agent in either tetrahydrofuran (THF) or



**Scheme 3.** *Reagents and conditions:* i, MCPBA–MeOH (25 °C for 1 h); ii, PhSeCl–MeOH–$Et_3N$ (25 °C for 2 h); iii, $H_2O_2$–MeOH or THF (25 °C for 1 h)

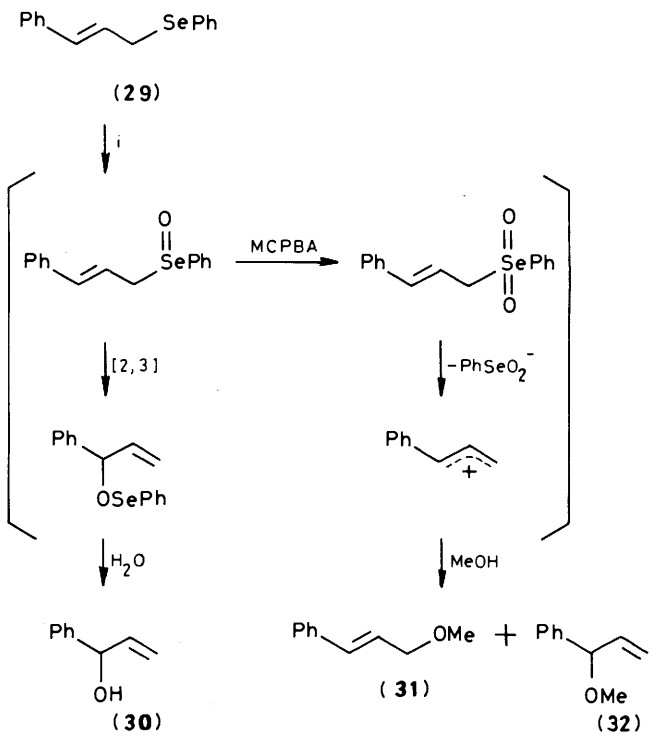
methanol (see Scheme 3). In the MCPBA oxidation of the selenides (**22**), (**24**), and (**27**), on the other hand, substitution of the PhSe moiety by the methoxy group occurred without ring-contraction to give the corresponding α,β-dimethoxyalkanes (**23**), (**25**), and (**28**), respectively (see Scheme 4). Treatment of (**24**) with 5 equiv. of $H_2O_2$ in THF gave only the expected selenoxide



**Scheme 4.** *Reagents and conditions:* i, ii, and iii—see Scheme 3.

elimination product (**26**). Analysis of the products obtained by replacement of PhSe by MeO in the *trans*-compounds (**24**) and (**27**) showed that scrambling had occurred, mixtures of the *cis*- and *trans*-isomers in the ratios 58:42 and 40:60 (*cis*/*trans*), respectively, being obtained.

Oxidation of the allylic selenides (**29**) with 2—5 equiv. of MCPBA produced a rearranged allylic alcohol (**30**) in a high yield (>90%) together with small amounts of cinnamyl methyl ether (**31**) and its isomer (**32**). This means that a [2,3]sigmatropic rearrangement of the selenoxide is much faster than oxidation for the selenone and also that the attack of methanol on allylic selenone may involve an allylic cation intermediate, although this is a very minor process (see Scheme 5).*



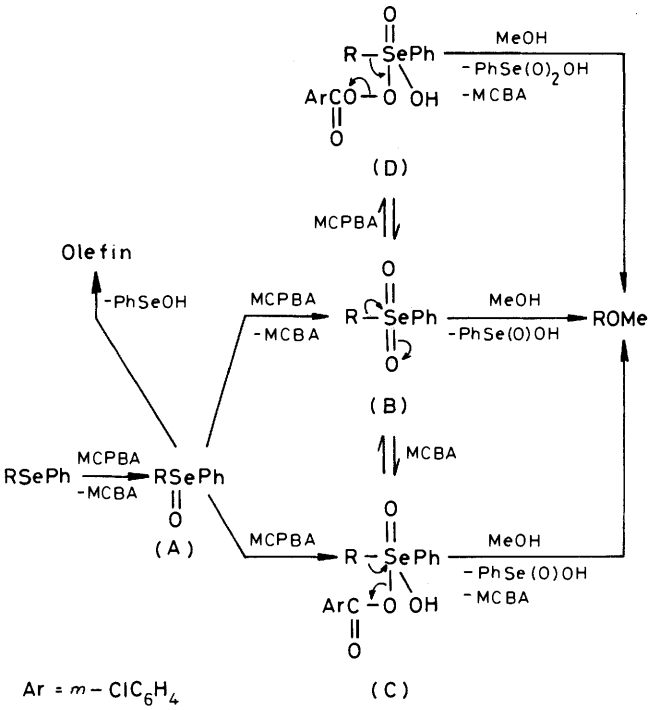
**Scheme 5.** *Reagents and conditions:* i, MCPBA–MeOH (25 °C for 1 h)

Our observation on the relationship between the MCPBA/selenide ratio and the nature of the products (Table 1) suggests that in the oxidation with 1 equiv. of MCPBA the selenoxide (A) is formed from the selenide followed by selenoxide elimination to give the olefin; use of either 2 equiv. or an excess of MCPBA appears, however, to give a further oxidized species, the selenone (B), in which methanol attack occurs to give the product ether (see Scheme 6).† Other oxidizing agents such as $H_2O_2$, $NaIO_4$, Bu$^t$OOH, and ozone may not be strong enough to afford the selenone and thus olefin was the sole product in these cases even when an excess of

* For a [2,3]sigmatropic rearrangement of allylic selenoxides and related reactions, see, for example, ref. 1*a*, pp. 102—113. It has been described how, when (**29**) was oxidized in ethanol using $H_2O_2$, a mixture of materials was obtained including unrearranged alcohol and ethers, the product ratio being unspecified.

† The stoicheiometry of the reaction by use of 2 equiv. of MCPBA is as follows:

$$RSePh + 2MCPBA + MeOH \longrightarrow ROMe + 2MCBA + PhSe(O)OH$$




**Scheme 6.**

reagent was used.* On the other hand, MCPBA may be a stronger reagent since, for example, it has already been shown that 2 equiv. of MCPBA reacted with a vinylic selenide to afford a vinylic selenone in methanol at room temperature.[3] The product composition in Table 1 shows that the oxidation of (A) to (B) by MCPBA is solvent-dependent and much faster in methanol than in other alcohols and dichloromethane. It has been shown that with dichloromethane as the solvent the oxidation of methyl phenyl selenide with 3 equiv. of MCPBA gave only methyl phenyl selenoxide, methyl phenyl selenone being obtained only when more than 3 equiv. of MCPBA was used;[9] we found that the treatment of methyl phenyl selenide with 2 equiv. of MCPBA in methanol at 20—25 °C for 1—2 h afforded dimethyl ether as the only detectable product (by g.l.c.; its amount could not be determined accurately), the starting selenide, its selenoxide and its selenone not being detected after the reaction. In order to explain the facile transformation of C–Se into C–O bonds described here, we propose that both the *meta*-chlorobenzoic acid (MCBA) generated and MCPBA itself have a catalytic effect in the formation of such species as (C) and (D), respectively, by addition to (B) (see Scheme 6). In (C) and (D), the phenylselenium function is a much better leaving group than the phenylselenonyl ($PhSeO_2$) group because of the electron-withdrawing ability of the $ArCO_2$ (Ar = *m*-chlorophenyl) group. From (B) and (C) phenylseleninic acid [PhSe(O)OH] is produced by methanol attack, while phenylselenonic acid [$PhSe(O)_2OH$] can be eliminated from (D) without a valence change of selenium.† Phenylselenium species were recovered, in part, as diphenyl diselenide by a work-up procedure involving aqueous $Na_2S_2O_3$ as a reducing agent. The C–Se bond fission seems to occur heterolytically, accompanied by a concerted attack of methanol or, in several cases, by phenyl migration or ring-contraction before the methanol attack.

* The addition of acid may improve the oxidizing ability of these reagents as evidenced in the case of $H_2O_2$ (see Table 1). The acid may also work as a catalyst to facilitate the C–Se bond fission of selenone as clarified in a similar reaction of tellurone (see Table 3).

There is also the possibility of the intermediacy of a carbocationic species in some cases as evidenced by the scrambling of the stereochemistry in a cyclic system and also by the formation of isomeric methyl ethers from an allylic selenide. As to the selenone, Sharpless *et al.*[2] have suggested it as an intermediate in the oxidation of (**1**) with $H_2O_2$–$CF_3CO_2H$ in acetic acid to afford dodecyl acetate and, similarly, Kuwajima *et al.*[3] have proposed it as an intermediate in oxetane formation on oxidation of a vinylic selenide by MCPBA. Furthermore, the $PhSeO_2$ group of vinylic selenones is known to be a sufficiently good leaving group as to be substituted with another nucleophile.[11]

*Alkyl Phenyl Tellurides and Telluroxides.*—In a typical reaction, a methanol solution of dodecyl phenyl telluride (**33**) and MCPBA (3 equiv.) was stirred at 25 °C for 1 h. After work-up, g.l.c. analysis indicated the presence of dodecyl methyl ether (**2**; R = Me) and the complete absence of dodec-1-ene, anisole, phenol, and dodecan-1-ol; (**2**; R = Me) was isolated in 50% yield by simple distillation (see Scheme 7). The yield was not improved by increasing the amount of MCPBA and the reaction was quite slow in ethanol and propan-2-ol. When a similar reaction was carried out with dodecyl phenyl telluroxide monohydrate (**34**) in methanol, prepared from (**33**) according to Detty's method,[12] the yield of (**2**; R = Me) was much higher (95% isolated yield) and 2 equiv. of MCPBA was shown to be sufficient (see Scheme 7). In this case, the reaction proceeded quite smoothly even in other alcohols such as ethanol, propan-1-ol, and propan-2-ol to give the corresponding compound (**2**). MCPBA Seems to be a specific oxidizing agent for this transformation, as in the above described selenide cases, and the treatment of (**34**) with excess of other oxidants such as Bu$^t$OOH, $NaIO_4$, $H_2O_2$, and ozone failed to give any (**2**; R = Me) under the conditions (MeOH/25 °C/1 h) where 95% of it was produced by use of MCPBA. It should be added that the oxidation of (**34**) with $H_2O_2$ proceeded very slowly to give (**2**) and was accelerated by the addition of acids such as $CF_3CO_2H$, $HClO_4$, or $BF_3$·$Et_2O$. In a combination such as $H_2O_2/CF_3CO_2H$ the *in situ* formation of $CF_3CO_3H$ is possible and this might well be a much more effective oxidant than $H_2O_2$. Next, the reactivity of dodecyl phenyl tellurone dihydrate (**35**), prepared by oxidation of (**34**) with $NaIO_4$ in aqueous methanol according to Cava's method,[13] was examined. The treatment of (**35**) with MCPBA in methanol afforded (**2**; R = Me) in high yield (see Scheme 7), while (**35**) itself is stable in methanol and failed to give any (**2**) even after being stirred in methanol for 3 days at 25 °C. Although both (**33**) and (**34**) are stable in methanol even in the presence of strong acid and failed to give any (**2**), the tellurone (**35**) afforded (**2**) in moderate yield in the presence of various acids such as $CF_3CO_2H$, $CF_3SO_3H$, $HNO_3$, and *m*-chlorobenzoic acid (MCBA). Typical results for the oxidation of (**33**), (**34**), and (**35**) are summarized in Table 3.

The application of this reaction to several other primary and

† Since selenonic acids are known to be strong oxidizing agents,[10] phenylselenonic acid may oxidize the MCBA produced to MCPBA or oxidize a selenoxide to a selenone. In the latter case the catalytic cycle shown below is expected. This cycle can explain why 2 equiv. of MCPBA is enough for the formation of alkyl methyl ether even if the reaction proceeded *via* (D).

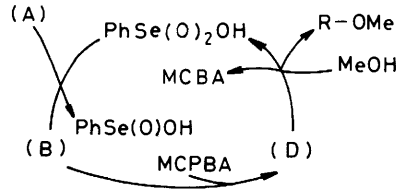
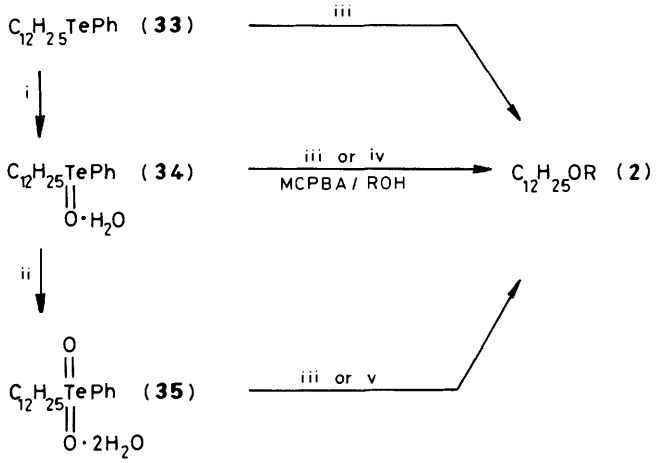


**Table 3.** Oxidation of dodecyl phenyl telluride (**33**), telluroxide (**34**), and tellurone (**35**) in alcohol[a]

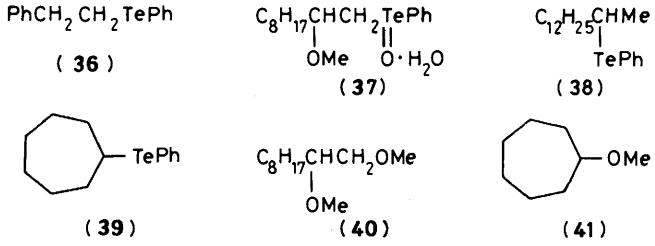
| Compd. | Alcohol R in ROH | React. time (h) | Oxidizing agent (equiv.)[b] | | Acid (equiv.)[b] | | Yield of (**2**) (%)[c] |
|---|---|---|---|---|---|---|---|
| (**33**) | Me | 1 | MCPBA | 1 | | | 18 |
| (**33**) | Me | 1 | MCPBA | 3 | | | 50[d] |
| (**33**) | Et | 1 | MCPBA | 3 | | | 10 |
| (**33**) | Pr$^i$ | 1 | MCPBA | 3 | | | Trace |
| (**34**) | Me | 1 | MCPBA | 1 | | | 45 |
| (**34**) | Me | 1 | MCPBA | 2 | | | 95[d] |
| (**34**) | Et | 1 | MCPBA | 2 | | | 70[d] |
| (**34**) | Pr$^i$ | 1 | MCPBA | 2 | | | 70[d] |
| (**34**) | Pr | 1 | MCPBA | 2 | | | 65[d] |
| (**34**) | Me | 1 | *t*-BuOOH | 5 | | | 0 |
| (**34**) | Me/H[e] | 1 | $NaIO_4$ | 5 | | | 0 |
| (**34**) | Me | 1 | $H_2O_2$ | 5 | | | 0 |
| (**34**) | Me | 1 | Ozone excess | | | | 0 |
| (**34**) | Me | 24 | $H_2O_2$ | 5 | | | 26 |
| (**34**) | Me | 72 | $H_2O_2$ | 5 | | | 20 |
| (**34**) | Me | 1 | $H_2O_2$ | 5 | $CF_3CO_2H$ | 5 | 0 |
| (**34**) | Me | 24 | $H_2O_2$ | 5 | $CF_3CO_2H$ | 5 | 88 |
| (**34**) | Me | 72 | $H_2O_2$ | 5 | $HClO_4$ | 5 | 60 |
| (**34**) | Me | 72 | $H_2O_2$ | 5 | $BF_3$·$Et_2O$ | 5 | 68 |
| (**34**) | Me | 24 | $H_2O_2$ | 5 | $HCO_2H$ | 5 | 32 |
| (**34**) | Me | 24 | $H_2O_2$ | 5 | $Ac_2O$ | 5 | 47 |
| (**34**) | Me | 1 | | | MCBA[f] | 5 | 0 |
| (**35**) | Me | 72 | | | | | 0 |
| (**35**) | Me | 1 | MCPBA | 2 | | | 87 |
| (**35**) | Me | 1 | MCPBA | 1 | | | 32 |
| (**35**) | Me | 1 | | | MCBA | 5 | 15 |
| (**35**) | Me | 1 | | | $CF_3CO_2H$ | 5 | 36 |
| (**35**) | Me | 72 | | | $CF_3CO_2H$ | 5 | 32 |
| (**35**) | Me | 1 | | | $HNO_3$ | 5 | 22 |
| (**35**) | Me | 1 | | | $CF_3SO_3H$ | 5 | 35 |

[a] Te compound (1 mmol), alcohol (10 ml), at 25 °C. In the case of isolation of the product, Te compound (2 mmol) was used. [b] Mole equivalent to Te compound employed. [c] G.l.c. yield with an internal standard. [d] Isolated yield [e] MeOH (5 ml)/$H_2O$ (5 ml). [f] *m*-Chlorobenzoic acid.



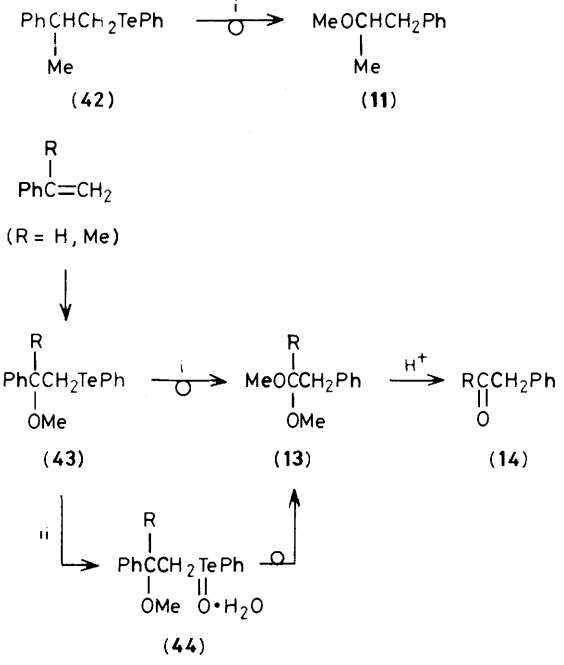

**Scheme 7.** *Reagents and conditions:* i, $Br_2$–$CCl_4$ (0 °C) and aqueous 0.5M-NaOH (20—25 °C for 1 h); ii, $NaIO_4$–aqueous MeOH (20—25 °C for 20 h); iii, MCPBA–ROH (25 °C for 1 h); iv, $H_2O_2$–acid–MeOH (25 °C for 24—72 h); v, acid–MeOH (25 °C for 1 h)

secondary alkyl phenyl tellurides and telluroxides such as (**36**) (**37**), (**38**), and (**39**) afforded the corresponding methyl ethers (**7**), (**40**), (**9**), and (**41**), respectively. In the case of tellurides the use of an excess of MCPBA was generally necessary to obtain a good yield of the product ether, otherwise the olefin formation




prevailed as exemplifed by a quantitative formation of styrene from (**36**) by use of 1 equiv. of MCPBA. In the oxidation of (**39**), the formation of the expected ether (**41**) was always accompanied by cycloheptene oxide even when a large excess of MCPBA (5—10 equiv.) was used. In this case the telluroxide elimination is probably faster than in other cases. We confirmed separately that cycloheptene can be oxidized readily to the oxide by MCPBA under the reaction conditions used.

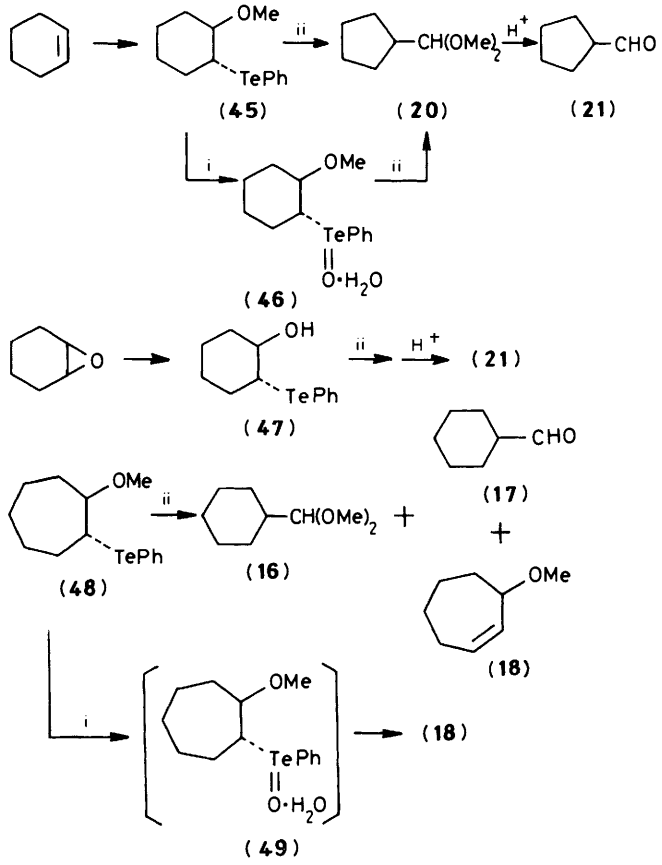
When the phenyl group was situated at a vicinal position to the phenyltellurium function, as in the cases of (**42**), (**43**), and (**44**), the replacement of the tellurium function by the methoxy group was accompanied by phenyl migration as in the cases of the corresponding selenides (see Scheme 8). All reactions




**Scheme 8.** *Reagents and conditions:* i, MCPBA–ROH (25 °C for 1 h); ii, $Br_2$–$CCl_4$ (0 °C) and aqueous 0.5M-NaOH (20—25 °C for 1 h)

proceeded very rapidly by use of a stoicheiometric amount of MCPBA (10 min are generally enough) and the product yields were very high.

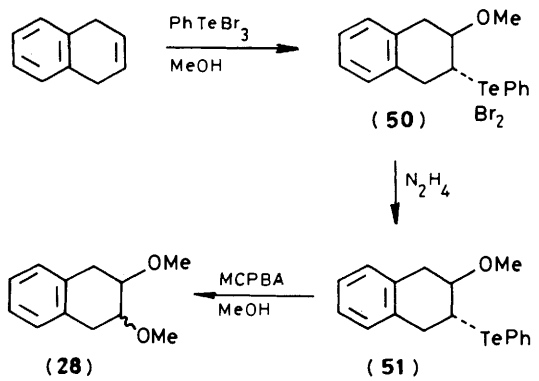
Treatment of the methoxytelluration products of cyclohexene and cycloheptene [(**45**) and (**48**)], where the methoxy group is situated at a vicinal position, with 2—5 equiv. of MCPBA readily afforded the dimethyl acetals of the ring-contracted cyclic aldehydes, (**20**) and (**16**), respectively in high yields (see Scheme 9). The oxidation of the β-hydroxy telluride (**47**) proceeded similarly to give (**21**) in a good yield after acid hydrolysis together with a small amount of cyclohexanone. In the oxidation of (**48**) using 1 equiv. of MCPBA, the allylic ether (**18**) was the major product with no formation of (**16**). The formation of (**18**) is expected from the intervention of the unstable cycloheptyl telluroxide (**49**) followed by rapid



**Scheme 9.** *Reagents and conditions:* i, $Br_2$–$CCl_4$ (0 °C) and aqueous 0.5M-NaOH (20—25 °C for 1 h); ii, MCPBA–ROH (25 °C for 1 h)

telluroxide elimination.[6] In contrast, the cyclohexyl telluroxide (**46**) is both stable and isolable and gave none of the corresponding allylic ether; ready ring-contraction occurred however on treatment with 1 equiv. of MCPBA. In contrast to the oxidation of (**34**), such oxidants as $NaIO_4$, $H_2O_2$, and Bu$^t$OOH also promoted the ring-contraction reaction of (**45**), (**47**), and (**48**), but a large excess of the oxidant was generally necessary; the product yields were, however, slightly lower in all cases compared with those of the MCPBA oxidation.

In contrast to the oxidation of (**45**), (**47**), and (**48**), the treatment of the *trans*-telluride (**51**) with MCPBA afforded a mixture of *cis*- and *trans*-(**28**) (*cis*:*trans* = 28:72) together with several minor unidentified products; no products arising from ring-contraction and the telluroxide elimination were observed. The result shows that the replacement of the PhTe moiety by the

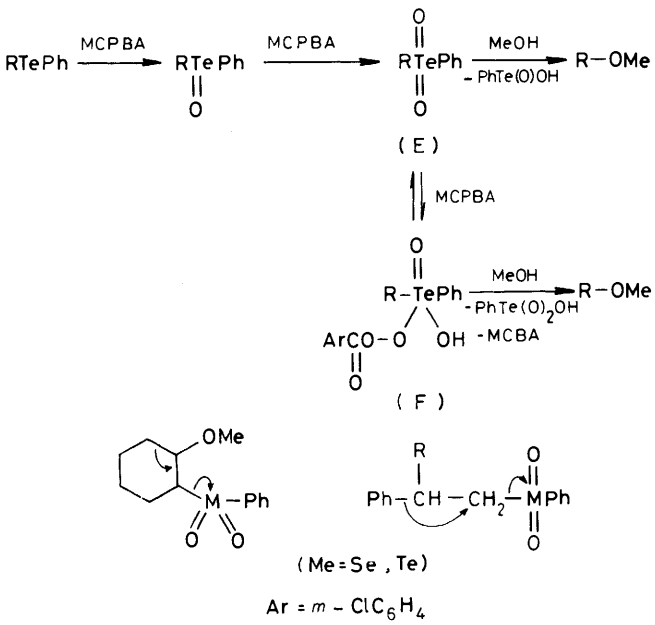


**Scheme 10.**

**Table 4.** Oxidation of various alkyl phenyl tellurides and telluroxides with some oxidants in methanol[a]

| Te compound | mmol | MCPBA (equiv.)[b] | Product and yield (%)[c] | |
|---|---|---|---|---|
| (**33**) | 2 | 3 | (**2**; R = Me) | 50[d] |
| (**34**) | 2 | 2 | (**2**; R = Me) | 95[d] |
| (**36**) | 2 | 5 | (**7**) | 67,[d] Styrene 14 |
| (**36**) | 1 | 1 | Styrene | 100 |
| (**37**) | 2 | 2 | (**40**) | 84[d] |
| (**38**) | 2 | 5 | (**9**) | 86[d] |
| (**39**) | 1 | 5 | (**41**) | 45, Cycloheptene oxide 45 |
| (**42**) | 2 | 3 | (**11**) | 90[d] |
| (**43**; R = H) | 2 | 2 | (**13**) | 90[d] |
| (**44**; R = H) | 2 | 1 | (**13**) | 73[d] |
| (**44**; R = Me) | 1 | 1 | (**14**) | 84 |
| (**45**) | 1 | 2 | (**20**) | 77 |
| (**45**) | 1 | 5[e] | (**21**) | 75[f] |
| (**46**) | 1 | 1 | (**20**) | 84 |
| (**46**) | 2 | 2[e] | (**20**) | 70[d] |
| (**47**) | 1 | 5 | (**21**) | 77,[f] Cyclohexanone 2 |
| (**47**) | 1 | 10 | (**21**) | 74,[f] Cyclohexanone 10 |
| (**48**) | 1 | 5 | (**16**) | 90 |
| (**48**) | 1 | 1 | (**17**) | 6, (**18**) 54 |
| (**48**) | 1 | 10[e] | (**16**) | 35, (**17**) 60, (**18**) 10 |
| (**48**) | 1 | 1[e] | (**18**) | 40 |
| (**48**) | 1 | 10[g] | (**16**) | 54, (**17**) 13, (**18**) 12 |
| (**48**) | 1 | 10[h] | (**16**) | 62, (**17**) 13, (**18**) 25 |
| (**51**) | 5 | 3 | (**28**) | 54 (*cis*/*trans* = 28:72) |

[a] At 20—25 °C. [b] Mole equivalent to Te compound employed. [c] G.l.c. yield. [d] Isolated yield. [e] $NaIO_4$ as the oxidant. [f] After hydrolysis with aqueous HCl. [g] $H_2O_2$ as the oxidant. [h] t-Butyl hydroperoxide as the oxidant.



**Scheme 11.**

methoxy group is non-stereospecific as in the case of the corresponding selenide (Scheme 10). All results are shown in Table 4.

From the relationship between the MCPBA/telluride or telluroxide ratio and the products, this oxidation appears to proceed *via* a process similar to that proposed for the selenides (Scheme 11). It appears to involve organotellurium compounds of a higher oxidation state to tellurium and the alkyl phenyl

tellurone (E) is the most plausible candidate for such an intermediate, the $PhTe(O)_2$ function working as a good leaving group as has been suggested for the corresponding selenium function of $PhSe(O)_2$. In some cases the former function may not be strong enough as a leaving group to give products, as exemplified by the experimental results that (**35**) itself is stable in methanol, but readily affords the product ether in the presence of MCPBA. Therefore, it is possible that a tellurone analogue such as (F), formed by the addition of MCPBA to (E), may be involved as a reactive intermediate in which a strong electron-withdrawing ability of $ArCO_2$ provides the driving force for the heterolytic fission of the C–Te bond. The mild effect of acid in the oxidation of (**34**) with $H_2O_2$ and also in the transformation of (**35**) to (**2**) may be attributed to protonolysis on the oxygen atom of the Te=O moiety of (E; R = $C_{12}H_{25}$) or (**35**) which makes a heterolytic C–Te bond fission easier.

## Experimental

$^1H$ N.m.r. spectra were taken with JEOL JNM FX-100 (100 MHz), JEOL JNM-GX 400 (400 MHz) and Varian EM-360 (60 MHz) instruments on solutions, in $CDCl_3$ with $SiMe_4$ as an internal standard. $^{13}C$ N.m.r. spectra were taken at 25.1 MHz with a JEOLCO $^{13}C$ Fourier transform n.m.r. system (JNM FX-100) and were recorded on solutions, in $CDCl_3$ after 250—1 000 pulses with intervals of 2.7—2.8 s. I.r. spectra were recorded with JASCO IR-810 (400—4 000 $cm^{-1}$) spectrometer (KBr disk and neat). G.l.c. analyses were carried out using a Shimadzu 4CMPF apparatus on Silicone DCQF-1 (5 and 30%)–Chromosorb-W (1 m), PEG 6000 (25%)–Shimalite (1 m), and EGSS-X (3 and 15%)–Chromosorb-W (1 m) columns ($N_2$ as carrier gas). Melting points were determined with Shimadzu MM-2 micro melting point determination apparatus and were uncorrected. Ozonolysis was carried out using a Nippon Ozon Co. Type 0-3-2 apparatus.

Commercially available diphenyl diselenide (Aldrich), phenylseleninyl chloride (Nakarai Chemicals), *m*-chloroperbenzoic acid (Nakarai Chemicals, 80% purity), $H_2O_2$ (30%), Bu$^t$OOH (70%), $NaIO_4$, $NaBH_4$, NaH, and $PBr_3$ were used without further purification, while commercial organic compounds such as olefins, alcohols, and alkyl halides were distilled immediately before use. Reaction products such as dodec-1-ene, tetradec-1-ene, styrene, 1,1-dimethoxy-2-phenylethane (**13**; R = H), benzyl methyl ketone (**14**; R = Me), benzyl phenyl ketone (**14**; R = Ph), cyclohexane carbaldehyde (**17**), dimethyl ether, and cinnamaldehyde are commercially available for g.l.c. analyses. Cyclohexane carbaldehyde dimethyl acetal (**16**) was prepared by acetalization of the aldehyde (**17**) in methanol in the presence of a few drops of $HClO_4$. The preparations of tetradec-2-enes and 3-methoxycycloheptene (**18**) have previously been reported.[6] Authentic methyl ethers [dodecyl methyl ether (**2**; R = Me), methyl 2-phenylethyl ether (**7**), 2-methoxytetradecane (**9**), 2-methoxy-1-phenylpropane (**11**), methyl 2-phenylpropyl ether, cinnamyl methyl ether (**31**), and 3-methoxy-3-phenylpropene (**32**)] were prepared by a reported method[14] by methylation of the corresponding commercial alcohols with MeI and NaH in anhydrous tetrahydrofuran at 20—25 °C for 5 h. Compounds [dodecyl ethyl ether (**2**; R = Et), dodecyl propyl ether (**2**; R = Pr$^n$), and dodecyl isopropyl ether (**2**; R = Pr$^i$)] were similarly prepared from dodecanol using the corresponding alkyl iodides instead of MeI. Compounds [cyclopentanecarbaldehyde (**21**; R = H) and cyclopentyl methyl ketone (**21**; R = Me)] were prepared by oxidation of cyclohexene and 1-methylcyclohexene with $Tl(NO_3)_3 \cdot 3H_2O$ in methanol respectively.[15]

*Preparation of Alkyl Phenyl Selenide.*—(a) *From alkyl halide.* According to the reported method[16] the following selenides were prepared from alkyl bromide (10 mmol), diphenyl diselenide (5 mmol), and $NaBH_4$ (15 mmol) in EtOH (25 ml) at room temperature for 1—2 h under a $N_2$ atmosphere. Each selenide was isolated by column chromatography on silica gel (elution with hexane), its characterization and the isolated yield being as follows: (**8**) is a new compound.

*Dodecyl phenyl selenide* (**1**). A yellow oil (90%), $\delta_H$ (100 MHz) 0.88 (3 H, t), 1.1—1.8 (20 H, m), 2.88 (2 H, t), 7.1—7.3 (3 H, m), and 7.3—7.5 (2 H, m).

2-*Phenylethyl phenyl selenide* (**6**). A yellow oil (100%), $\delta_H$ (100 MHz) 2.8—3.2 (4 H, m), 7.0—7.3 (8 H, m), and 7.3—7.5 (2 H, m) (Found: C, 64.5; H, 5.5. Calc. for $C_{14}H_{14}Se$: C, 64.4; H, 5.4%).

*Tetradecan-2-yl phenyl selenide* (**8**). A yellow oil (80%), $\delta_H$ (100 MHz) 0.88 (3 H, t), 1.1—1.8 (22 H, m), 1.40 (3 H, d), 3.28 (1 H, sext.), 7.1—7.3 (3 H, m), and 7.4—7.6 (2 H, m) (Found: C, 68.4; H, 9.7. $C_{20}H_{34}Se$ requires C, 68.0; H, 9.7%).

2-*Phenylpropyl phenyl selenide* (**10**). A yellow oil (85%), $\delta_H$ (100 MHz) 1.37 (3 H, dt, *J* 7 and 2 Hz), 2.7—3.35 (3 H, m), 7.0—7.3 (3 H, m), and 7.3—7.5 (2 H, m); $\delta_C$ 21.7(q), 36.6(t), 40.3(d), 126.5(d), 126.6(d), 126.8(d), 128.4(d), 128.9(d), 130.8(s), 132.5(d), and 145.9(s) (Found: C, 65.5; H, 5.9. Calc. for $C_{15}H_{16}Se$: C, 65.45; H, 5.9%).

*Cinnamyl phenyl selenide* (**29**). A pale yellow solid (99%), m.p. 59—61 °C (from EtOH), $\delta_H$ (100 MHz) 3.45—3.85 (2 H, m), 6.1—6.4 (2 H, m), 7.1—7.3 (8 H, m), and 7.4—7.6 (2 H, m); $\nu_{max.}$(KBr) 1 480s, 968s, 750s, and 695s $cm^{-1}$ (Found: C, 65.9; H, 5.2. Calc. for $C_{15}H_{14}Se$: C, 65.9; H, 5.2%).

*Methyl phenyl selenide.* A yellow oil (95% by distillation), prepared by use of methyl iodide; $\delta_H$ (60 MHz) 2.30 (3 H, s), 7.0—7.4 (5 H, m).

(b) *From olefin.* β-Methoxyalkyl phenyl selenides [1-methoxy-1-phenyl-2-phenylselenoethane (**12**; R = H), *trans*-1-methoxy-2-phenylselenocycloheptane (**15**), *trans*-1-methoxy-2-phenylselenocyclohexane (**19**; R = H), and *trans*-1-methoxy-2-phenylselenocyclopentane (**22**)] were prepared by *trans*-methoxyselenation of the corresponding olefins by the reported method.[17] Other selenides were similarly prepared by mixing the olefin (10 mmol), PhSeCl (10 mmol), and methanol (20 ml) at 20—25 °C followed by the addition of $Et_3N$ (10 mmol) and by stirring the resulting mixture for 2 h. The characterization of new compounds, isolated in a pure form in over 90% yield by column chromatography on silica gel [elution with hexane–ethyl acetate (10:1)], is as follows.

2-*Methyl*-2-*methoxypentyl phenyl selenide* (**4**). A yellow oil, $\delta_H$ (100 MHz) 0.88 (3 H, t), 1.24 (3 H, s), 1.3—1.8 (4 H, m), 3.09 (2 H, d, *J* 1.5 Hz), 3.15 (3 H, s), 7.1—7.3 (3 H, m), and 7.35—7.6 (2 H, m) (Found: C, 57.7; H, 7.4. $C_{13}H_{20}OSe$ requires C, 57.6; H, 7.4%).

2-*Methoxy*-2-*phenylpropyl phenyl selenide* (**12**; R = Me). A yellow oil, $\delta_H$ (100 MHz) 1.68 (3 H, s), 3.08 (3 H, s), 3.24 (1 H, d, *J* 11.8 Hz), 3.41 (1 H, d, *J* 11.8 Hz), 7.0—7.2 (3 H, m), and 7.2—7.4 (7 H, m); $\delta_C$ 23.1(q), 42.4(t), 50.8(q), 78.9(s), 126.2(d), 126.5(d), 127.3(d), 128.2(d), 128.8(d), 131.4(s), 132.6(d), and 143.7(s) (Found: C, 62.9; H, 6.1. $C_{16}H_{18}OSe$ requires C, 62.95; H, 5.9%).

2,2-*Diphenyl*-2-*methoxyethyl phenyl selenide* (**12**; R = Ph). A pale yellow solid, m.p. 96—97 °C, $\delta_H$ (100 MHz) 3.10 (3 H, s), 3.92 (2 H, s), and 7.0—7.4 (15 H, m) (Found: C, 68.8; H, 5.5. $C_{21}H_{20}OSe$ requires C, 68.7; H, 5.5%).

2-*Methyl*-2-*methoxycyclohexyl phenyl selenide* (**19**; R = Me). A yellow oil, $\delta_H$ (100 MHz) 1.28 (3 H, s), 1.2—2.2 (8 H, m), 3.20 (3 H, s), 3.42 (1 H, dd, *J* 8 and 4 Hz), 7.1—7.3 (3 H, m), and 7.4—7.6 (2 H, m) (Found: C, 59.45; H, 7.05. $C_{14}H_{20}OSe$ requires C, 59.4; H, 7.1%).

trans-1-*Methoxy*-2-*phenylselenoindan* (**24**). A yellow oil, $\delta_H$ (100 MHz) 2.88 (1 H, dd, *J* 17 and 3.7 Hz), 3.31 (3 H, s), 3.51 (1 H, dd, *J* 17 and 7.2 Hz), 3.98 (1 H, ddd, *J* 7.2, 3.7, and 2.9 Hz), 4.75 (1 H, d, *J* 2.9 Hz), 7.0—7.4 (7 H, m), and 7.45—7.6 (2 H, m); $\delta_C$ 38.2(t), 41.5(d), 56.7(q), 89.9(d), 124.7(d), 125.4(d), 126.7(d), 127.4(d), 128.8(d), 128.9(d), 129.4(s), 134.0(d), 140.7(s),

and 142.0(s) (Found: C, 63.45; H. 5.3. $C_{16}H_{16}OSe$ requires C, 63.4; H, 5.3%).

trans-2-*Methoxy*-3-*phenylseleno*-1,2,3,4-*tetrahydronaphthalene* (**27**). A yellow oil, $\delta_H$ (400 MHz) 2.87 (1 H, dd, *J* 17.1 and 5.9 Hz), 2.95 (1 H, dd, *J* 16.6 and 7.1 Hz), 3.27 (1 H, dd, *J* 17.1 and 5.4 Hz), 3.32 (1 H, dd, *J* 16.6 and 4.9 Hz), 3.42 (3 H, s), 3.71 (1 H, ddd, *J* 7.1, 6.3, and 4.9 Hz), 3.78 (1 H, ddd, *J* 6.3, 5.9, and 5.4 Hz), 6.97—7.0 (1 H, m), 7.07—7.15 (3 H, m), 7.25—7.34 (3 H, m), and 7.58—7.64 (2 H, m); $\delta_C$ 33.0(t), 33.9(t), 42.3(d), 56.4(q), 78.6(d), 126.0(d), 126.2(d), 127.5(d), 128.4(d), 128.9(d), 129.1(d), 130.3(s), 133.4(s), 134.4(s), and 134.8(d) (Found: C, 64.5; H, 5.8. $C_{17}H_{18}OSe$ requires C, 64.35; H, 5.7%).

This compound was also prepared separately by the following procedure. First, 1,4-dihydronaphthalene oxide was produced by epoxidation of 1,4-dihydronaphthalene with MCPBA in ethyl acetate at −78 °C to 20 °C for 18 h. The resulting oxide solution was added to an ethanol solution of $(PhSe)_2$ and $NaBH_4$ at 0 °C and the mixture was stirred at 20—25 °C for 24 h. Work-up ($CH_2Cl_2$ as the extract), followed by column chromatography [$SiO_2$, hexane–ethyl acetate (5:1)], afforded *trans*-2-hydroxy-3-phenylseleno-1,2,3,4-tetrahydronaphthalene (66% isolated yield) as a semisolid. A tetrahydrofuran solution of this solid and then methyl iodide were added successively to a NaH–THF suspension at −78 °C and the mixture was stirred at −78 °C to room temperature for 1 h. The corresponding β-methoxy selenide was isolated in a yield of 76%, by work-up as above; the $^1H$ n.m.r. (400 MHz) spectrum of the product was in accord with its being the selenide (**27**).

*Oxidation of Selenides: General Procedure.*—To a colourless methanolic solution (10 ml) of the selenide (**1**) (0.33 g, 1 mmol) was added solid MCPBA (80% purity; 0.66 g, 3 mmol) at 25 °C and with stirring. The resulting solution was stirred for 1 h and then *ca.* 0.5M-$Na_2S_2O_3$ (20 ml) was added followed by saturated aqueous $NaHCO_3$ (100 ml). The mixture was extracted with diethyl ether (50 ml × 3) and the combined extracts dried ($MgSO_4$). G.l.c. analysis of the extract (using cyclododecene as an internal standard, Silicone DC QF-1 1 m column) showed the presence of dodec-1-ene (0.07 mmol, 7%) and dodecyl methyl ether (**2**; R = Me) (0.80 mmol, 80%). Removal of the solvent left a pale yellow oily residue which was distilled on a Kugelrohr distillation apparatus (Büchi GKR-50) to afford pure (**2**; R = Me) (0.12 g, 0.60 mmol); $\delta_H$ (60 MHz) 0.83 (3 H, t), 1.0—1.8 (21 H, m), 3.23 (3 H, s), and 3.1—3.4 (2 H, m). Several other methyl ethers which were isolated by Kugelrohr distillation and/or preparative t.l.c. (silica gel) and characterized by $^1H$ n.m.r. are as follows: (**5**) and (**28**) are new compounds.

1,2-*Dimethoxy*-2-*methylpentane* (**5**). $\delta_H$ (60 MHz) 0.8—1.8 (7 H, m), 1.16 (3 H, s), 3.20 (3 H, s), 3.27 (2 H, s), and 3.36 (3 H, s).

1,2-*Dimethoxycyclopentane* (**23**). $\delta_H$ (60 MHz) 1.50—2.0 (6 H, m), 3.30 (6 H, s), and 3.4—3.6 (2 H, m); $\delta_C$ 21.4(t), 29.7(t), 56.8(q), 86.4(d) for a major component and 19.1(t), 27.3(t), 57.1(q), 82.1(d) for a minor one.

1,2-*Dimethoxyindane* (**25**). Each isomer was isolated in pure form by preparative t.l.c. of the product mixture [elution with hexane–ethyl acetate (4:1)]. The *trans*-isomer was also prepared separately by the following steps (10 mmol scale); MCPBA oxidation of indene in methanol at −78 to 20 °C, acid hydrolysis by $HClO_4$, and methylation of the *trans*-1-methoxy-2-hydroxyindan so produced with MeI–NaH in THF at 0—25 °C (56% overall isolated yield). Its $^1H$ n.m.r. pattern is quite similar to that of *trans*-methoxyselenation product of indene (**24**). *trans*-Isomer: $\delta_H$ (100 MHz)[18] 2.77 (1 H, dd, *J* 16.1 and 5.5 Hz), 3.30 (1 H, dd, *J* 16.1 and 6.9 Hz), 3.44 (3 H, s), 3.55 (3 H, s), 4.05 (1 H, ddd, *J* 6.9, 5.5, and 4.1 Hz), 4.74 (1 H, d, *J* 4.1 Hz), and 7.2 (4 H, m); $\delta_C$ 36.0(t), 57.1(q), 57.1(q), 87.2(d), 88.3(d), 125.0(d), 125.0(d), 126.8(d), 128.6(d), 139.9(s), and 140.4(s). *cis*-Isomer: $\delta_H$ (100 MHz)[18] 3.06 (1 H, d, *J* 7.1 Hz), 3.08 (1 H, d, *J* 7.1 Hz), 3.41 (3 H, s), 3.50 (3 H, s), 4.05 (1 H, ddd, *J* 7.1, 7.1, and 4.9 Hz), 4.60 (1 H, d, *J* 4.9 Hz), 7.1 (4 H, m); $\delta_C$ 35.6(t), 56.3(q), 57.4(q), 81.9(d), 82.4(d), 125.4(d), 125.9(d), 126.4(d), 129.0(d), 139.8(s), and 140.9(s).

3-*Methoxyindene* (**26**). $\delta_H$ (60 MHz) 3.10 (3 H, s), 4.91 (1 H, d, *J* 2 Hz), 6.20 (1 H, dd, *J* 6 and 2 Hz), 6.57 (1 H, d, *J* 6 Hz), and 6.9—7.2 (4 H, m).

2,3-*Dimethoxy*-1,2,3,4-*tetrahydronaphthalene* (**28**). Each isomer was isolated in a pure form and the *trans*-isomer was also prepared separately (57% overall isolated yield) as in the case of the ether (**25**). *trans*-Isomer: $\delta_H$ (100 MHz) 2.8—2.9 (2 H, m), 2.9—3.0 (2 H, m), 3.40 (6 H, s), 3.5—3.7 (2 H, m), and 7.0 (4 H, m); $\delta_C$ 32.1(q), 57.0(q), 78.5(d), 126.1(d), 128.7(d), and 133.8(s). *cis*-Isomer: $\delta_H$ (100 MHz) 2.8—3.1 (4 H, m), 3.40 (6 H, s), 3.7—3.8 (2 H, m), and 7.0 (4 H, m); $\delta_C$ 31.5(t), 56.7(q), 76.8(d), 125.9(d), 129.0(d), and 133.5(s).

*Oxidation of Cinnamyl Phenyl Selenide* (**29**).—According to the general procedure described above, the selenide (**29**) (1 mmol) was treated with MCPBA (2 mmol) in methanol. G.l.c. analysis (using cinnamyl alcohol as an internal standard, Silicone DCQF-1 1 m column) of the ether extract revealed the presence of 1-phenylprop-2-enol (**30**) (96%) and small amounts of cinnamyl methyl ether (**31**) (2%) and 3-methoxy-3-phenylpropene (**32**) (2%). Almost the same result was obtained using 5 equiv. of MCPBA. For the isolation of (**30**), a 5-times scale reaction was carried out. Distillation in a Kugelrohr apparatus gave 0.60 g (90%) of (**30**): $\delta_H$ (100 MHz) 2.20 (1 H, br s), 5.15 (1 H, d, *J* 9 Hz), 5.15 (1 H, d, *J* 9 Hz), 5.28 (1 H, dt, *J* 19 and 1.5 Hz), 5.80—6.20 (1 H, m), and 7.1—7.4 (5 H, m); $\nu_{max.}$(neat) 3 370s, 1 025s, 990s, 930s, 760s, and 700s $cm^{-1}$.

Authentic samples of (**31**) and (**32**) for g.l.c. analysis were prepared almost quantitatively by methylation of cinnamyl alcohol and (**30**) respectively.[14] Compound (**31**): $\delta_H$ (100 MHz) 3.32 (3 H, s), 4.02 (2 H, dd, *J* 6 and 1.5 Hz), 6.20 (1 H, dt, *J* 15.5 and 6 Hz), 6.56 (1 H, dt, *J* 15.5 and 1.5 Hz), and 7.1—7.4 (5 H, m). Compound (**32**): $\delta_H$ (100 MHz) 3.30 (3 H, s), 4.56 (1 H, dt, *J* 6 and 1 Hz), 5.16 (1 H, ddd, *J* 10, 2.5, and 1 Hz), 5.24 (1 H, ddd, *J* 18, 2.5, and 1 Hz), 5.90 (1 H, ddd, *J* 18, 10, and 6 Hz), and 7.2—7.4 (5 H, m).

*Preparation of Alkyl Phenyl Tellurides and Telluroxides. From Alkyl Halide.*—According to the method already described[6] the tellurides [dodecyl phenyl telluride (**33**), 2-phenylethyl phenyl telluride (**36**), tetradecan-1-yl phenyl telluride (**38**), cycloheptyl phenyl telluride (**39**), 2-phenylpropyl phenyl telluride (**42**)] were prepared from the corresponding alkyl bromide (10 mmol), diphenyl ditelluride (5 mmol), and $NaBH_4$ (15 mmol) in ethanol (25 ml) at reflux temperature for 1—3 h under $N_2$ atmosphere. Each organotellurium compound was converted into the corresponding dibromide by treatment with bromine and isolated by column chromatography on $SiO_2$ [elution with hexane–ethyl acetate (10:1 to 5:1)]. The dibromide was converted back into the corresponding telluride by reduction with $N_2H_4$ just before use for MCPBA oxidation. It was also converted into the telluroxide by treatment with aqueous NaOH. The characterization of new compounds (**36**) and (**42**) is as follows. That of (**33**), (**34**), (**38**), and (**39**) has already been reported.[6]

*Phenyl*(2-*phenylethyl*)*tellurium dibromide* [*dibromide of* (**36**)]. A yellow solid, m.p. 105—106 °C, 95% isolated yield; $\delta_H$ (100 MHz) 3.48 (2 H, t), 4.04 (2 H, t), 7.2—7.3 (5 H, m). 7.3—7.5 (3 H, m), and 8.0—8.2 (2 H, m) (Found: C, 35.6; H, 3.0. $C_{14}H_{14}Br_2Te$ requires C, 35.8; H, 3.0%).

*Phenyl*(2-*phenylpropyl*)*tellurium dibromide* [*dibromide of* (**42**)]. A yellow solid, m.p. 120—121 °C, 93% isolated yield; $\delta_H$ (100 MHz) 1.52 (3 H, d), 3.8—4.2 (3 H, m), 7.2—7.4 (3 H, m), 7.8—8.1 (2 H, m); $\delta_C$ 22.5(q), 36.7(d), 58.9(t), 127.0(d), 127.7(d), 128.5(s),

128.9(d), 129.7(d), 131.2(d), 134.1(d), and 143.0(s) (Found: C, 37.3; H, 3.4. $C_{15}H_{16}Br_2Te$ requires C, 37.25; H, 3.3%).

*From Olefin.*—β-Methoxyalkyltellurium dibromides were prepared by *trans*-methoxytelluration of the corresponding olefins with $PhTeBr_3$ in methanol as described previously.[19] The tellurides [2-methoxy-2-phenylethyl phenyl telluride (**43**; R = H), 2-methoxy-2-phenylpropyl phenyl telluride (**43**; R = Me), *trans*-1-methoxy-2-phenyltellurocyclohexane (**45**), and *trans*-1-methoxy-2-phenyltellurocycloheptane (**48**)] were prepared by reducing the produced dibromides with $N_2H_4$ just before use for MCPBA oxidation, while the telluroxides [2-methoxydecyl phenyl telluroxide hydrate (**37**), 2-methoxy-2-phenylethyl phenyl telluroxide hydrate (**44**; R = H), 2-methoxy-2-phenylpropyl phenyl telluroxide hydrate (**44**; R = Me), and 2-methoxycyclohexyl phenyl telluroxide hydrate (**46**)] were prepared by the treatment of the dibromides with aqueous NaOH. The characterization of the dibromides of (**43**; R = H), (**43**; R = Me), (**45**), and (**48**) and the telluroxides has already been shown.[17] The following compounds, (**50**) and (**51**), are new.

2-*Methoxy*-1,2,3,4-*tetrahydro*-3-*naphthyl Phenyl Telluride Dibromide* (**50**). To a homogeneous solution of $PhTeBr_3$ (3.0 g, 7.0 mmol) in MeOH (5 ml) was added a MeOH (2 ml) solution of 1,4-dihydronaphthalene (1.0 g, 7.7 mmol); the resulting mixture was stirred at reflux temperature for 3h during which period a yellow solid was precipitated. The mixture was cooled to room temperature, and the precipitated solid collected by filtration, washed with chilled methanol, and dried *in vacuo*: 1.92 g, 3.5 mmol, 50% yield, m.p. 130—131 °C; $\delta_H$ (100 MHz) 2.84 (1 H, dd, *J* 16 and 11 Hz), 3.00 (1 H, dd, *J* 16 and 5.5 Hz), 3.4—3.7 (2 H, m), 3.58 (3 H, s), 4.28 (1 H, ddd, *J* 11, 11, and 5.5 Hz), 4.62 (1 H, ddd, *J* 11, 11, and 5.5 Hz), 6.8—7.2 (4 H, m), 7.4—7.6 (3 H, m), and 8.2—8.4 (2 H, m); $\delta_C$ 31.5(t), 35.6(t), 57.2(q), 67.3(d), 76.1(d), 124.1(s), 126.6(d), 128.6(d), 129.5(d), 129.7(d), 131.3(d), 132.3(s), 134.1(d), and 136.5(d) (Found: C, 38.9; H, 3.6. $C_{17}H_{18}Br_2OTe$ requires C, 38.8; H, 3.45%).

trans-2-*Methoxy*-3-*phenyltelluro*-1,2,3,4-*tetrahydronaphthalene* (**51**). To a heterogeneous EtOH solution (10 ml) of the *telluride dibromide* (**50**) (1.05 g, 2 mmol) was added $N_2H_4 \cdot H_2O$ (0.25 g, 20 mmol) drop by drop. When the evolution of $N_2$ had ceased and the solution had become homogeneous, the mixture was diluted with brine and extracted with ether (30 ml × 3). The combined extracts were dried ($MgSO_4$) and evaporated to leave an oily residue which was purified by column chromatography on silica gel [hexane–ethyl acetate (10:1 to 5:1)]: a yellow oil, 100% yield, $\delta_H$ (100 MHz) 2.76 (1 H, dd, *J* 17 and 7 Hz), 3.0—3.2 (3 H, m), 3.35 (3 H, s), 3.68 (1 H, ddd, *J* 8, 7, and 5 Hz), 3.96 (1 H, ddd, *J* 8, 8, and 6 Hz), 6.7—7.3 (7 H, m), and 7.7—7.9 (2 H, m); $\delta_C$ 26.8(d), 34.3(t), 36.4(t), 56.3(q), 80.4(d), 110.9(s), 125.9(d), 126.1(d), 128.0(d), 128.9(d), 129.2(d), 133.5(s), 135.5(s), and 140.5(d) (Found: C, 54.7; H, 4.8. $C_{17}H_{18}OTe$ requires C, 55.8; H, 5.0%).

*Preparation of* trans-1-*Hydroxy*-2-*phenyltellurocyclohexane* (**47**).—An ethanol (10 ml) solution of cyclohexene oxide (0.98 g, 10 mmol) was injected by a syringe into a colourless ethanol solution (10 ml) of diphenyl ditelluride (2.05 g, 5 mmol) and $NaBH_4$ (0.55 g, 15 mmol) under $N_2$ and with stirring. The resulting mixture was stirred at reflux temperature for 1 h, poured into aqueous NaCl after being cooled down to room temperature, and extracted with $CHCl_3$ (50 ml × 3). The extract was dried ($MgSO_4$) and the solvent evaporated to leave an orange liquid which was purified by column chromatography on silica gel [elution with hexane–ethyl acetate (5:1 to 3:1)] to afford pure (**47**) (2.25 g, 7.4 mmol, 74% yield) as a yellow oil.[19]

*Preparation of Dodecyl Phenyl Tellurone Dihydrate* (**35**).—To a heterogeneous solution of dodecyl phenyl telluroxide hydrate (**34**) (2.03 g, 5 mmol) in methanol (20 ml) was added an aqueous solution (20 ml of distilled water) of $NaIO_4$ (2.14 g, 10 mmol) at room temperature. A white precipitate was formed and the resulting mixture was stirred for 24 h; it was then diluted with water (150 ml). The solution was extracted with $CHCl_3$ (50 ml × 3) and the combined extracts were dried ($MgSO_4$) and evaporated to leave a pale brown syrup; $\delta_H$ (60 MHz) 0.8—1.5 (23 H, m), 1.8—2.0 (4 H, br m), 3.0—3.4 (2 H, br m), 7.2—7.5 (3 H, br m), and 7.8—8.1 (2 H, br m); $\nu_{max.}$(neat) 3 300br, 3 060, 2 940s, 2 860s, 1 570, 1 465s, 1 420s, 1 380, 1 300, 1 180, 1 105, 1 060, 1 020, 1 000, 738s, 688s, and 600br s $cm^{-1}$ (Found: C, 48.7; H, 7.1. $C_{18}H_{30}O_2Te \cdot 2H_2O$ requires C, 48.9; H, 7.75%).

*Oxidation of Telluroxide with* m-*Chloroperbenzoic acid (MCPBA). General Procedure.*—To a heterogeneous MeOH (10 ml) solution of the telluroxide (**34**) (0.82 g, 2 mmol) was added solid MCPBA (80% purity; 0.88 g, 4 mmol) at 25 °C and with stirring. The resulting solution became homogeneous after 1 h, at which time it was treated with aqueous $Na_2S_2O_3$ followed by aqueous $NaHCO_3$. The mixture was extracted with diethyl ether (30 ml × 3), and the combined extracts were dried ($MgSO_4$), and evaporated to leave a pale yellow oily residue which was purified by column chromatography on $SiO_2$ [elution with hexane–ethyl acetate (5:1)] to afford the pure ether (**2**; R = Me) (0.38 g, 1.9 mmol, 95% yield). The alkyl ethers [(**2**; R = Et), (**2**; R = $Pr^n$), and (**2**; R = $Pr^i$)] were also isolated by column chromatography [$SiO_2$, hexane–ethyl acetate (5:1)].

*Oxidation of Telluroxide with* $H_2O_2$ *in the Presence of Acid: General Procedure.*—To a stirred and homogeneous mixture of the telluroxide (**34**) (0.41 g, 1 mmol) and $CF_3CO_2H$ (0.52 g, 5 mmol) in MeOH (10 ml) was added $H_2O_2$ (0.57 g, 5 mmol, 30%) at 25 °C. The resulting mixture was stirred for 24 h and then poured into aqueous $NaHCO_3$. The mixture was extracted with diethyl ether (30 ml × 3), and the combined extracts were dried ($MgSO_4$). G.l.c. analysis of the extract showed the presence of the ether (**2**; R = Me) (0.18 g, 0.88 mmol) with cyclododecene as an internal standard.

*Reaction of Dodecyl Phenyl Tellurone Dihydrate* (**35**) *with Acid.*—A homogeneous mixture of the *tellurone* (**35**) (0.44 g, 1 mmol) and $CF_3CO_2H$ (0.52 g, 5 mmol) in MeOH (10 ml) was stirred at room temperature for 1 h, and then poured into aqueous $NaHCO_3$. The mixture was extracted with diethyl ether (30 ml × 3), and the extract was dried over $MgSO_4$. G.l.c. analysis of the extract showed the presence of the ether (**2**; R = Me) (0.072 g, 0.36 mmol, 36% yield).

*Oxidation of* trans-2-*Methoxy*-3-*phenyltelluro*-1,2,3,4-*tetrahydronaphthalene* (**51**).—According to a general procedure described above, the *telluride* (**51**) (1.85 g, 5 mmol) was treated with MCPBA (3.3 g, 15 mmol) in MeOH (30 ml). G.l.c. analysis of the extract revealed the presence of *trans*- and *cis*-(**28**) (*trans*/*cis* = 72 : 28) and several unidentified compounds. Each isomer of (**28**) was isolated in a pure form by preparative t.l.c. [$SiO_2$; developed by hexane–ethyl acetate (4:1), *trans*-isomer has a larger $R_f$ value]; *trans*-isomer (0.37 g, 1.94 mmol) and *cis*-isomer (0.15 g, 1.76 mmol), 54% yield.

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