Registry No.—1, 4420-74-0; 2, 31001-77-1; 5, 2530-87-2; 6, 35112-74-4; 1-dodecanethiol, 112-55-0; dodecyl chloride, 112-52-7; dodecyl disulfide, 2757-37-1; 3-chloropropylmethyldimethoxysilane, 18171-19-2; 1-hexanethiol, 111-31-9; *n*-hexyl chloride, 544-10-5; 1,2-ethanedithiol, 540-63-6; 1,2-dibromoethane, 106-93-4; benzyl mercaptan, 100-53-8; benzyl chloride, 100-44-7; cyclohexanethiol, 1569-69-3; bromocyclohexane, 108-85-0; bis(trimethoxysilylpropyl) polysulfide, 40550-17-2; dihexyl disulfide, 10496-15-8; 1-chlorohexane, 544-10-5.

References and Notes

(1) S. Patai, Ed., "The Chemistry of the Thiol Group", Wiley, NewYork, N.Y., 1974, Vol 1, pp 180–182.
(2) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Chemical Publishing Co., New York, N.Y., 1958, Vol 1, pp 25–29, 66.
(3) L. Scheflin and C. R. McCrosky, *J. Am. Chem. Soc.*, **54**, 193 (1932).
(4) J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **71**, 428 (1897).
(5) S. D. Simpson, *Can. J. Res., Sect. B*, **25**, 20 (1947).
(6) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012, (1964).
(7) Arthur V. Tobolsky, Ed., "The Chemistry of Sulfides", Wiley, New York, N.Y., 1968, p 224.
(8) B. D. Vineyard, *J. Org. Chem.*, **31**, 601 (1966).
(9) D. Welti and D. Whittaker, *J. Chem. Soc.*, 4372 (1962).
(10) G. A. Gornowicz and J. L. Speier, *Mech. React. Sulfur Compd.*, **3**, 53 (1968).

Synthetic Applications of Arylselenenic and Arylseleninic Acids. Conversion of Olefins to Allylic Alcohols and Epoxides

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A new direct (one reaction vessel) route from olefins to rearranged allylic alcohols has been developed. It involves electrophilic addition of phenylselenenic acid (PhSeOH) to the olefin. The phenylselenenic acid is generated in situ by comproportionation of phenylseleninic acid ($PhSeO_2H$) and diphenyl diselenide (PhSeSePh). The addition of PhSeOH to trisubstituted olefins is highly regioselective. A new procedure for the oxidation/elimination of alkyl phenyl selenides is described. It employs *tert*-butyl hydroperoxide in place of hydrogen peroxide and avoids the secondary epoxidation process which can be a problem with the latter oxidant. Arylseleninic acids were found to be effective catalysts for the epoxidation of olefins with hydrogen peroxide. However, attempts to achieve asymmetric epoxidations by employing optically active arylseleninic acids as catalysts met with failure. A simple procedure for generating DMAC solutions of sodium selenocyanate by direct reaction of sodium cyanide with selenium metal is described. NaSeCN so generated is used in the preparation of *o*-nitrophenyl selenocyanate.

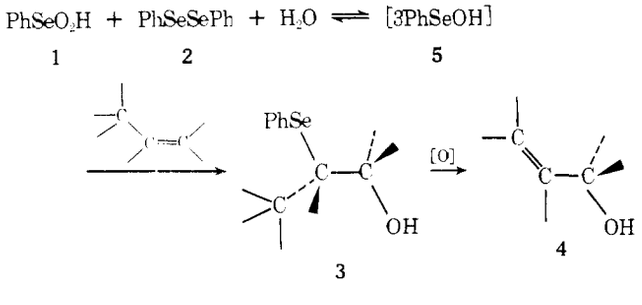
Olefins to Allylic Alcohols

We report here a new procedure for the conversion of an olefin to a rearranged allylic alcohol. The process involves addition of the olefin to a methylene chloride solution containing both phenylseleninic acid (**1**) and diphenyl diselenide (**2**). As shown in Scheme I a β-hydroxyphenyl selenide adduct **3** is produced,[2,3] and subsequent oxidation of this adduct, in the same reaction vessel, leads to the allylic alcohol **4** in good yield. The adduct **3** probably arises by electrophilic addition of phenylselenenic acid (**5**)[4] to the olefin.

The putative intermediate **5** is thought to be generated in situ by the redox reaction between seleninic acid **1** and diselenide **2.** Going from left to right, as shown in Scheme I, this process is formally a comproportionation. The equilibrium is apparently driven by capture of the selenenic acid **5** by the olefin.

The addition of aromatic selenenic acid derivatives (ArSeX) to olefins was discovered by Hölzle and Jenny.[5] Our group,[6] Reich's group,[7] and Clive[8] demonstrated the utility of such additions for synthesis of allylically functionalized alkenes.

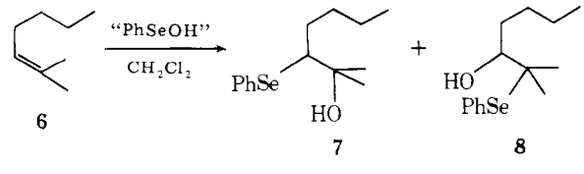
Scheme I



However, the direct addition of "PhSeOH" to olefins had not been accomplished.[9] In addition to producing allylic alcohols directly, the new procedure offers high regioselectivity (Table I, entries 4 and 5) in circumstances where the earlier reagents (e.g. CH_3CO_2SePh[6] and CF_3CO_2SePh[7,8]) afford almost 1:1 mixtures of regioisomers.

The general procedure employed for addition of "PhSeOH" to olefins calls for generation of phenylseleninic acid (**1**) in situ by addition of the appropriate (i.e., that required to generate an ~1:1 mixture of **1** and **2**) amount of 30% hydrogen peroxide to a methylene chloride solution of diphenyl diselenide (**2**).[10] When this initial oxidation is complete anhydrous $MgSO_4$ is added to sequester most of the excess water. The addition of $MgSO_4$ has two important, if unanticipated, effects on the course of the subsequent reaction with the olefin: (1) both the rates of formation and the yields of the adducts **3** are increased; (2) in the case of trisubstituted olefins the Markownikoff regioselectivity is complete (whereas when anhydrous $MgSO_4$ is omitted some of the anti-Markownikoff regioisomer is also formed). For example, as shown in Scheme II addition of "PhSeOH" to 2-methyl-2-heptene (**6**) in the presence of anhydrous $MgSO_4$ gave adduct **7** exclusively, whereas when

Scheme II



with $MgSO_4$ 100:0
without $MgSO_4$ 85:15

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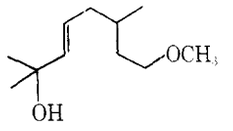
Table I. Olefins to Allylic Alcohols

Entry	Olefin	Registry no.	Allylic alcohol, % yield[a]
1	(*E*)-4-Octene	14850-23-8	(*E*)-3-Octen-5-ol, 88
2	(*Z*)-4-Octene	7642-15-1	(*E*)-3-Octen-5-ol, 84
3	Cyclooctene	931-88-4	**10**, 83
4	Citronellol methyl ether	55915-70-3	**9**, 87
5	1-Methylcyclohexene	591-49-1	**17**, 33[b]

[a] The reported yields are for pure substances isolated by distillation. [b] In this case anhydrous chloramine-T was used in place of TBHP for oxidation/elimination of the hydroxyselenide adduct **15**.

the addition was performed in the absence of $MgSO_4$ some of the regioisomer **8** was also produced.

The second stage of this transformation, which is carried out in the same reaction vessel, is the oxidation of the hydroxy selenide adduct **3** to the corresponding selenoxide. The selenoxide is thermally unstable and eliminates PhSeOH (**5**) producing the desired allylic alcohol product **4**. Hydrogen peroxide has been the reagent most commonly employed for the oxidation/elimination of alkyl aryl selenides. However, we and others have encountered side reactions, principally overoxidation, associated with the use of H_2O_2 for the oxidative removal of phenylseleno moieties from organic structures. In the present case when the hydroxy selenide adducts **3** were oxidized with excess H_2O_2 the allylic alcohol products were sometimes further transformed to the corresponding epoxy alcohols. For cyclooctene this was a serious complication, but for the other examples in Table I it was less of a problem. For example, allylic alcohol **9** produced from citronellol methyl



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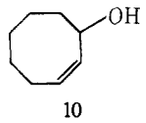

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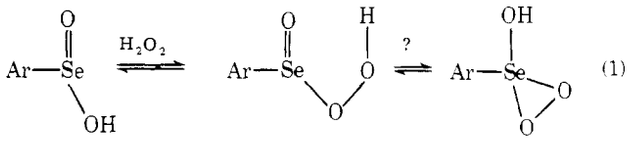
ether (entry 4) was very resistant to epoxidation. Even in the case of cyclooctene, allylic alcohol **10** could be isolated in good yield if only 2 molar equiv (based on diphenyl diselenide used) of H_2O_2 was employed. This is the calculated amount of H_2O_2 necessary to oxidize all the selenium(II) species to selenium(IV) species. However, under these conditions some diphenyl diselenide (**2**) always remains at the end of the reaction. This may be due in part to catalytic decomposition of some of the H_2O_2 by selenium species.[17] Separation of the yellow diselenide **2** from the allylic alcohol requires either a chromatography or a distillation. Thus convenience dictates the use of excess oxidant so that all the diphenyl diselenide is oxidized to phenylseleninic acid, which can be readily extracted into aqueous base.[11] We have found that *tert*-butyl hydroperoxide is an ideal oxidant for this purpose. It can be used in excess with no tendency for epoxidation of the olefinic products.

We have recently established the superiority of *tert*-butyl hydroperoxide over H_2O_2 for use in both OsO_4[12] and SeO_2[13] catalyzed oxidations of olefins. The success of this alkyl hydroperoxide in the present system is in keeping with its highly selective oxidizing properties. The presence of an alkyl group on one side of the peroxide linkage removes many of the reaction pathways which are open to H_2O_2. For example, the epoxidation process observed with H_2O_2 is almost certainly due to the formation of a peracid **12a** or its related cyclic peroxo isomer **12b** through the equilibrium given in eq 1.



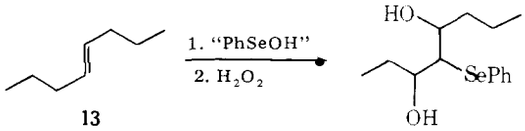
11 **12a** **12b**

We have shown that seleninic acids undergo facile exchange with ^{18}O-labeled water.[14] Specifically, it was found that an allylic seleninic acid underwent oxygen exchange with $H_2{}^{18}O$ much more rapidly than it underwent 2,3-sigmatropic rearrangement to the allylic alcohol.

Several other advantages which accrue from the use of *tert*-butyl hydroperoxide (TBHP) in place of H_2O_2 as the oxidant are worth mentioning. Unlike H_2O_2, TBHP reveals no tendancy to cause oxidative removal of the selenium from the aromatic ring in the phenylseleninic acid (**1**) by-product. Thus the seleninic acid **1** is recovered in high yield and then readily reduced to regenerate the starting diphenyl diselenide (**2**). Following a typical allylic alcohol preparation which employed 23.4 g (75 mmol) of diphenyl diselenide (**2**), reduction of the aqueous phenylseleninic acid containing extracts afforded 21.9 g (93% recovery) of diselenide **2** (mp 60.3–61.1 °C). This crude diselenide was sufficiently pure for reuse, but could be further purified by recrystallization from hexane.

Our attempts to recover the diselenide **2** in cases where H_2O_2 has been the oxidant have been less successful. As reported previously,[6] in a sequence beginning with 29.5 g of diselenide **2** only 15 g (51% recovery) was recovered by reduction of the aqueous extracts. We feel these poorer recoveries with H_2O_2 are due, at least in part, to the oxidative destruction of phenylseleninic acid mentioned above.[18] In support of this contention is the observation that reduction of aqueous extracts containing phenylseleninic acid, which has been exposed to excess H_2O_2, often leads to production of red selenium metal, in addition to the desired yellow diselenide **2**. The extent of seleninic acid decomposition varies with the amount of excess H_2O_2 and the period of exposure.[22] The problem can be alleviated by using only 2 molar equiv (based on diphenyl diselenide used) of H_2O_2, but this leads to the aforementioned product contamination by diselenide **2**.

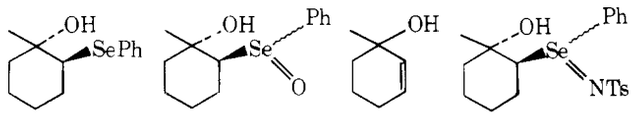
Both our group and Reich's[2,3] have encountered another important reason for the use of excess oxidant in the oxidation/elimination step. The initial product of syn elimination of an alkyl phenyl selenoxide is phenylselenenic acid (PhSeOH, **5**). As revealed in the present work and by Reich's recent results,[2,3] PhSeOH readily undergoes electrophilic addition to olefins. Thus it would be expected to add to the allylic alcohol being produced unless either disproportionation (Scheme I, **5** → **1** + **2**) or oxidation to phenylseleninic acid (**1**) occurred more rapidly. The presence of excess oxidant (H_2O_2 or TBHP) ensures rapid oxidation and prevents addition of PhSeOH to the product olefins. However, when excess oxidant is not utilized undesirable side reactions involving PhSeOH can be observed. This problem is more pronounced for some substrates than for others. For example, before it was found that excess TBHP could be used as the oxidant, we were trying to avoid the overoxidation problem (seleninic acid catalyzed epoxidation) by using only 2 molar equiv (based on diphenyl diselenide used) of H_2O_2. For 4-octene (**13**) this led to formation of substantial amounts of the diol selenide **14** (mp 77.9–78.6 °C, 48%). Diol **14** presumably arises by addition of



13 **14**

PhSeOH to the corresponding *E*-allylic alcohol. The addition seems to be regio- and stereoselective, since only one diastereomer was detected. However, the possibility that other isomers were present in small amounts was not rigorously excluded.

TBHP was highly successful as the oxidant for all the cases in Table I except for 1-methylcyclohexene (entry 5). In this case the selenoxide(s) **16** derived from the hydroxy selenide adduct **15** showed negligible tendency for elimination at room temperature. Even when the solvent was changed from CH_2Cl_2 to 1,2-dichloroethane, so that a reflux temperature of about 80 °C could be achieved, the yield of the desired allylic alcohol **17** was <10%. We had previously found[23] that the *p*-toluenesulfonylselenimide analogues of selenoxides elimi-



15 16 17 18

nate more readily than the selenoxides. Therefore the adduct **15**, which was isolated in 83% yield, was treated with 2 equiv of anhydrous chloramine-T in dichloroethane.[24] After stirring for several hours at room temperature the hydroxy selenide **15** had disappeared and two new compounds were apparent by TLC. Although these new substances were not isolated, they were presumably the two diastereomeric selenimides **18**. Probably due to the steric congestion in this system, even these selenimides were slow to undergo thermal elimination. However, after refluxing for 2 h allylic alcohol **17** and 1,2-epoxy-1-methylcyclohexane[25] were produced in a 2:1 ratio. Chromatography (to remove the epoxide) and distillation afforded allylic alcohol **17** in 40% yield from adduct **15** or in 33% yield based on the starting olefin. It is interesting to note that one (the less polar isomer on TLC) of the selenimides **18** disappeared more rapidly upon refluxing than the other. This observation parallels that of Jones, Mundy, and Whitehouse on the pyrolysis of a pair of sterically encumbered diastereomeric selenoxides.[26]

The general applicability of this new method (i.e., the use of 2 equiv of anhydrous chloramine-T in CH_2Cl_2 or $ClCH_2CH_2Cl$) for the oxidation/elimination of alkyl phenyl selenides has not been explored. However, it has an advantage over the phase-transfer procedure[23] utilizing chloramine-T in that there is no need to worry about separation of the phase-transfer agent (e.g. "Aliquat-336") from the products.

The other new procedure (i.e., TBHP in CH_2Cl_2) for oxidation/elimination of alkyl phenyl selenides has also not been investigated with regard to its general usefulness. However, we have made several observations worth mentioning here. The procedure offers no advantage over H_2O_2 for primary selenides. Only a trace of 1-dodecene is formed after exposure of 1-dodecyl phenyl selenide to excess TBHP in CH_2Cl_2 for 22 h. The problem does not lie in the rate of the oxidation step since TLC indicates that oxidation to the selenoxide is complete in 0.5–1 h. In the case of cyclododecyl phenyl selenide, exposure to TBHP in CH_2Cl_2 for 15 h at 25 °C resulted in formation of 92% cyclododecene (~1:1 mixture of *E* and *Z* isomers). By contrast, oxidation of cyclododecyl phenyl selenide with H_2O_2 in THF at 25 °C led rapidly (<1 h) to cyclododecene in 94% yield.[14] If this latter reaction mixture were allowed to stand for 15 h at 25 °C, then a substantial amount of epoxidation occurred (after 15 h: 58% cyclododecene and 38% cyclododecene oxide).[27] Since polar solvents such as THF disfavor epoxidation, one could anticipate that epoxidation would have been more of a complication had CH_2Cl_2 been the solvent. Actually, this problem of further epoxidation does not seem to exist for monosubstituted olefins and is only rarely experienced with disubstituted olefins. It is in cases involving tri- and especially tetrasubstituted olefins where further epoxidation is difficult to prevent if H_2O_2 is used as the oxidant.[20,21] It is in these latter circumstances that the use of TBHP for the oxidation/elimination step should provide special advantage. Baeyer–Villiger oxidation of certain ketones to lactones is another complication which has been encountered when H_2O_2 is employed as oxidant.[23,28] The use of TBHP as oxidant in such cases would be worth investigating.

As can be seen from the preceding discussion *tert*-butyl hydroperoxide (TBHP) should in many cases prove superior to hydrogen peroxide for the oxidation/elimination of alkyl phenyl selenides.[29] Because TBHP is a gentle oxidant, we generally use an excess to promote rapid completion of the desired oxidation. For example, in the present work 268 mmol were employed when 150 mmol is the theoretical amount required to convert all the selenium species to phenylseleninic acid (**1**). Since TBHP is not as sensitive[30] to catalytic decomposition by selenium species as is H_2O_2,[17] the excess oxidant remains at the end of the reaction. Moreover, TBHP is (unlike H_2O_2) more soluble in organic solvents than in water, and is therefore not removed by aqueous washes[31] during workup. There are a variety of ways of dealing with this excess TBHP. One approach is to perform a nonreductive workup and then remove it under vacuum (1 mm or better) at around 25–35 °C. However, for large-scale (>1 mol) reactions prior reduction is recommended. *Aqueous bisulfite has often been used for this purpose,*[12,32] *but we strongly recommend that this reductant be avoided whenever possible.* We have recently found that its use has a deleterious effect on isolated yields, especially when the desired products are epoxides[33] or allylic alcohols.[13] The effect is particularly severe if one attempts to distill the product of a large-scale (>1 mol) reaction; typically, the product will polymerize exothermically during attempted distillation. This complication is easily avoided by using dimethyl sulfide[34] (in the presence of a catalytic amount of acetic acid[35]) as the reductant in place of bisulfite. We now use this Me_2S procedure for all large-scale reductions of TBHP.[13]

In the present work aqueous ferrous sulfate is employed as the reducing agent. This method works well; reduction occurs more rapidly than with Me_2S and it has the added advantage of being ordorless. However, we do not recommend use of this $Fe^{II}SO_4$ reduction technique for larger scale (>0.1 mol) reactions. Even though the reductions involve a two-phase (ether–water) system, the Fe^{II}/Fe^{III} couple is well known[36] to catalyze free-radical decomposition of alkyl hydroperoxides, suggesting obvious possibilities for trouble. If larger scale applications of this reduction technique were to be explored, it would seem advisable to employ inverse addition (i.e., slowly add the ethereal organic extract containing the TBHP to a well-stirred aqueous $FeSO_4$ solution).[37]

Olefins to Epoxides

There has been long-standing interest in discovering a means for direct use of H_2O_2 for epoxidation of olefins. An obvious approach is the in situ generation of carboxylic peracids. Unfortunately the exchange process between H_2O_2 and a carboxylic acid requires strong acid catalysis and is therefore incompatible with the desired epoxide products. For example, formic acid (a strong enough acid to catalyze its own exchange with H_2O_2) is often used for conversion of an olefin to a vicinal diol in the presence of H_2O_2; the intermediate epoxides cannot be isolated under these conditions.[38] Since there is a trend toward more facile exchange processes upon descending the rows in the periodic table, one finds that the in situ formation of peracids (**20a**, e.g. M = Se) and peroxides (**20b**, e.g. M = V,

Table II. Epoxidation of Cyclooctene

Entry	Catalyst[a]	Registry no.	Equiv of 30% H_2O_2	$MgSO_4$[b]	Time, h	Epoxide/olefin[c]
1	SeO_2 (control)		2	−	16	2:98
2	**1**	6996-92-5	2	−	16	65:35
3	**26**	65252-75-7	2.2	−	20	79:21
4	**26**		2.2	+	20	99.7:0.3
5	**24**	15001-52-2	2	−	16	0.4:99.6
6	**25**	65252-76-8	2	−	16	0.3:99.7
7	**27**	20753-53-1	2.2	−	16	40:60
8	**28**	33350-70-8	2.2	−	16	50:50
9	**22**	56790-59-1	2.2	−	20	91:9
10	**23**	65252-77-9	2.2	−	20	96:4
11	**23**		2.2	+	20	99.6:0.4

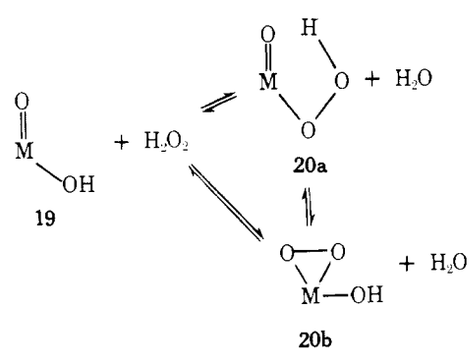
[a] In each case 10% of the seleninic acid catalyst was employed and the solvent was always CH_2Cl_2. [b] A + sign indicates that excess anhydrous $MgSO_4$ was added. [c] Indicates the GLC determined ratio of product to starting material; in all cases the mass balance is ~100%.

Table III. Epoxidation of Citronellol Methyl Ether

Entry	Catalyst[a]	Equiv of H_2O_2 (% strength)	$MgSO_4$	Time, h	Epoxide/olefin[b]
1	**22**	2 (30)	−	16	84:16
2	**22**	2 (30)	+	16	100:0
3	**22**	2 (98)	−	16	100:0
4	**23**	2 (30)	−	16	69:31
5	**23**	2 (30)	+	16	100:0

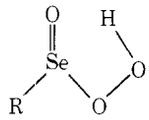
[a] In each case 1.0% of the seleninic acid catalyst was used. [b] Same as footnote *c* in Table II except that with this olefin the mass balances were only ~90%.

Scheme III



Mo, W) occurs under very mild conditions[39] in the presence of H_2O_2 (Scheme III). In fact, the elements indicated above (V, Mo, W, Se) are among those which are known to be active catalysts for the epoxidation of olefins with H_2O_2.[40,42] However, these catalytic systems are very poor for the epoxidation of simple, isolated olefins.[40b,40c] Of particular interest for the present work are the reports in which SeO_2 was observed to catalyze epoxidation of olefins.

In his pioneering studies of allylic oxidation with SeO_2, Guillemonat had investigated the use of H_2O_2 as a source of the oxygen in the reaction.[41] However, the only products he obtained were vicinal diols and no allylic oxidation products. The formation of diols from olefins and SeO_2 in the presence of H_2O_2 was later studied as a reaction in its own right.[42] Tanaka eventually showed that epoxides were the initial products in this reaction, and that diols arose from ring opening under the usual reaction conditions.[43] Perselenious acid (**21a**) was proposed as the active epoxidizing species.



21a, R = OH
b, R = Ph

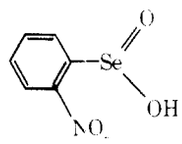
Very recently Grieco has reported epoxidation of olefins by H_2O_2 in the presence of a stoichiometric quantity of phenylseleninic acid (**1**).[21] He suggests that the corresponding peracid **21b** is the active reagent. We had discovered this same epoxidizing activity[16,18] in the course of our early[15] experiments on organoselenium reagents. It was further observed that stoichiometric use of the seleninic acid is not necessary, and that arylseleninic acids showed activity as phase-transfer catalysts for the epoxidation of olefins with H_2O_2.[18] However, the lifetime of the seleninic acid (**1**) itself as a catalyst was disappointing for the acid was being degraded to SeO_2 and presumably some oxidized organic fragment.[18] This decomposition process may be due to Baeyer–Villiger type rearrangement[19] of the peracid **12a** or its peroxo isomer **12b.**

Reich's group has also encountered these seleninic acid catalyzed epoxidations.[20] We report here those aspects of our results on this new epoxidation procedure which are most relevant to its preparative potential.

In addition to phenylseleninic acid (**1**), we have also investigated the seleninic acids **22–30** as epoxidation catalysts. With the exception of the alkyl seleninic acid **24** and *o*-hydroxycarbonylphenylseleninic acid (**25**), all of these compounds exhibited some activity as epoxidation catalysts (Table II). Methylene chloride is an especially good solvent for these epoxidations.

The results in Table II for the epoxidation of cyclooctene reveal the relative effectiveness of the various seleninic acid catalysts. The *o*-nitrophenylseleninic acid (**22**) and the 2,4-dinitrophenylseleninic acid (**23**) are clearly the best catalysts.[44] The presence of water has a deleterious effect on the epoxidation process.[45] Good results were obtained using 30% H_2O_2 and anhydrous $MgSO_4$ to scavenge the excess water.[46] High-strength (98%) H_2O_2 was also successful, but seemed less desirable from the point of view of both safety and convenience.

Table III gives results obtained using the nitroseleninic acids **22** and **23** as catalysts for the epoxidation of a trisubstituted olefin (citronellol methyl ether); in this case 1.0% catalyst was used. The combination of 30% H_2O_2 and anhy-



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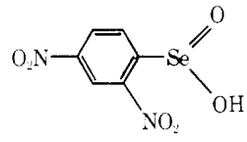

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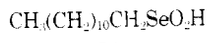

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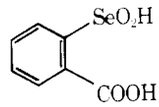

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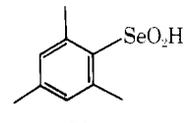

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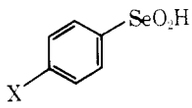
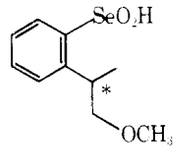


27, X = Cl
28, X = NO_2



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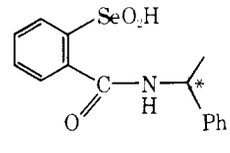


30

drous $MgSO_4$ works well (entries 2 and 5), but if 98% H_2O_2 is employed (entry 3) use of $MgSO_4$ is obviated.

In Table IV are shown the results of performing the catalytic epoxidation on a preparative scale. The yields given are for pure, distilled epoxides. Only for cyclooctene is the yield near quantitative. In the case of (*E*)-5-decene and 2-methyl-2-heptene the isolated yields are somewhat below the ~95% value that one would expect to be able to obtain by careful epoxidation of these olefins with carboxylic peracids. The simplicity of the procedure and the fact that H_2O_2 is less expensive than peracetic and perbenzoic acids (the most commonly used reagents for large scale laboratory epoxidations) are attractive aspects of these catalytic epoxidations.

It is always of interest to explore the behavior of a new epoxidizing reagent with olefinic alcohols. These substrates (especially allylic alcohols) are well known for undergoing highly selective epoxidations with both carboxylic peracids[47] and with alkyl hydroperoxides in the presence of vanadium and molybdenum catalysts.[32] As shown in Scheme IV epoxidation of 2-cyclohexen-1-ol (**31**) occurs almost randomly giving a 3:2 mixture of the *syn*- (**32**) and *anti*- (**33**) epoxy alcohols. This contrasts with the highly stereoselective syn epoxidation of **31** by carboxylic peracids[47] and by transition metal–alkyl hydroperoxide reagents.[32] Similarly, geraniol (**34**) affords a 2:1 mixture of epoxy alcohols **35** and **36.** This resembles the result with carboxylic peracids,[32a] but contrasts with the highly regioselective epoxidation (**34** → **36**) achieved with alkyl hydroperoxides in the presence of vanadium or molybdenum catalysts.[32a] This result differs somewhat from that of Grieco and co-workers using a stoichiometric quantity of phenylseleninic acid (**1**) and H_2O_2 in protic solvents.[21] They report a 5:1 mixture of epoxy alcohols **35** and **36.** This difference in regioselectivity probably arises from the difference in the seleninic acids and the solvents which were employed. In any case it appears that arylperoxyseleninic acids (**12a**) are unique[48] among epoxidizing agents in that they exhibit little, if any, regio- or stereoselectivity in epoxidations of allylic alcohols.

Scheme IV. Epoxidation of Allylic Alcohols

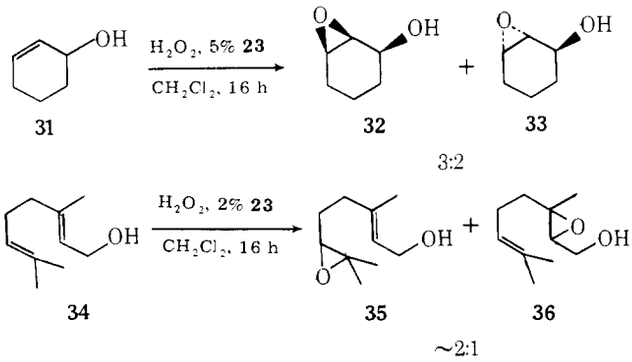


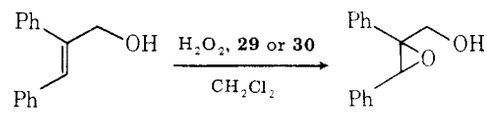
Table IV. Preparative Scale Epoxidations

Olefin	Registry no.	Catalyst (%)[a]	% yield[b] of epoxide
Cyclooctene		**23** (5)	95
(*E*)-5-Decene	7433-56-9	**22** (5)	90
2-Methyl-2-heptene	627-97-4	**22** (0.5)	81

[a] The figure in parentheses indicates the percentage of seleninic acid used. [b] The reported yields are for pure substances isolated by distillation.

In thinking of other possible unique features associated with these seleninic acid catalyzed epoxidations, it occurred to us that the putative active epoxidizing species, the arylperoxyseleninic acid **12a** or its peroxo isomer **12b,** was chiral.[49] Moreover, since the chirality resides at the selenium center this would place the asymmetry one atom closer to the site of oxygen transfer than can be achieved in chiral carboxylic peracids. Thus it seemed possible that chiral perseleninic acids might be superior to chiral percarboxylic acids[50] for the asymmetric epoxidation of olefins.

In order to test this idea the optically active seleninic acids **29** and **30** were synthesized.[51] The asymmetric centers in **29** and **30** are admittedly rather distant from the selenium; however, it was hoped that there would be considerable asymmetric induction in the exchange process (**11** ⇌ **12a**) leading to generation of the peroxyseleninic acid **12a.** Both seleninic acids **29** and **30** were effctive epoxidation catalysts in CH_2Cl_2 in the presence of H_2O_2.[51] However, when the prochiral allylic alcohol **37** was epoxidized using either **29** or **30** as catalyst the resulting epoxy alcohol **38** was racemic.[51,52]



37 38 (racemic)

Summary

1. A new direct (one reaction vessel) route from olefins to rearranged allylic alcohols has been developed. The only other direct process for this transformation involves reaction with singlet oxygen. The reactivity of singlet oxygen toward most disubstituted olefins is poor.[53] Singlet oxygen is often not regioselective in reactions with trisubstituted olefins,[53] whereas the addition of "PhSeOH" to trisubstituted olefins is highly regioselective.

2. A new procedure using *tert*-butyl hydroperoxide for the oxidation/elimination of alkyl phenyl selenides is described. It avoids the secondary epoxidation process, which can be a problem when H_2O_2 is used as the oxidant. The use of *tert*-butyl hydroperoxide in place of H_2O_2 also leads to much better recoveries of diphenyl diselenide when the byproduct phenylseleninic acid is reduced. In the present work *tert*-butyl hydroperoxide has proved an ideal reagent for the oxidation/elimination of β-hydroxyalkyl phenyl selenides. Its general applicability to other types of alkyl phenyl selenides has not been established but would seem to merit attention. In particular, whenever tri- or tetrasubstituted olefins are present in the molecule (either initially or are being formed

as a result of the selenoxide elimination) the use of *tert*-butyl hydroperoxide instead of H_2O_2 should avoid the epoxidation processes to which these types of olefins are especially prone.

3. It has been independently discovered by four groups,[20,21] including our own,[16,18] that arylseleninic acids catalyze the epoxidation of olefins by H_2O_2. A convenient catalytic procedure for the epoxidation of di-, tri-, and tetrasubstituted[54] olefins has been developed. The best catalysts found to date are *o*-nitrophenylseleninic acid (**22**) and 2,4-dinitrophenylseleninic acid (**23**); 0.5–5% of the catalyst is generally employed. The best solvent is CH_2Cl_2. The best general procedure involves use of 30% H_2O_2 in the presence of excess anhydrous $MgSO_4$.

Experimental Section

Reagent grade methylene chloride was employed, and for all applications it was dried by storage over 4-Å molecular sieves. *All reactions* were performed under an atmosphere of dry nitrogen in order to exclude atmospheric moisture. If the use of more than 12–13 g of anhydrous magnesium sulfate was required, then it was found that a mechanical stirrer should be used in place of a magnetic stirrer. The 90% *tert*-butyl hydroperoxide was obtained either from Aldrich or from the Lucidol Division of the Pennwalt Corp. Melting points and boiling points are uncorrected.

Sources of Olefins. The cyclooctene obtained from Aldrich is about 95% pure; it contains 4 or 5% of a nonolefinic impurity. The citronellol methyl ether was prepared by methylation (NaH, CH_3I, DMF) of an old sample of Aldrich citronellol and was >95% pure. The citronellol now sold by Aldrich is of much lower (~70%) purity. The other olefins [1-methylcyclohexene, 2-methyl-2-heptene, (*E*)-4-octene, (*Z*)-4-octene, and (*E*)-5-decene] were obtained from Chemical Samples and are all 96–99% pure.

Sources of Organoselenium Reagents and Catalysts. Diphenyl diselenide (PhSeSePh, **2**) is available from Aldrich; however, the material used here was prepared according to our published procedure.[55] *This procedure*[55] *gives full experimental details for preparation of PhSeSePh on a 1-mol scale.*

The *o*-nitrophenylseleninic acid (**22**) is the most generally useful epoxidation catalyst and therefore full details for an improved preparation of the corresponding selenocyanate and diselenide are given below. It should be noted that only in the case of seleninic acids **1**[56] and **24**[57] were the seleninic acids themselves actually used as the catalysts. In all other instances the catalysts were added in the form of their diselenides. It is well known[56] that diselenides are oxidized to seleninic acids in the presence of hydrogen peroxide. The diselenides corresponding to seleninic acids **23**,[58] **25**,[59] **26**,[60] **27**,[55] and **28**[61] were prepared according to the cited literature procedures.[62]

A Simple Procedure for in Situ Generation of Sodium Selenocyanate. The method[63] commonly used for preparing pure potassium selenocyanate or sodium selenocyanate is not very appealing. Therefore we have developed a simple procedure[64] for generating a *N,N*-dimethylacetamide (DMAC) solution of KSeCN or NaSeCN which should in many cases obviate the need for preparing the pure substance: anhydrous DMAC (75 mL) was degassed by bubbling nitrogen through it for 15 min. The reaction vessel containing the DMAC was maintained under a positive pressure of nitrogen, and 7.90 g (0.10 mol) of powdered gray selenium metal and 5.24 g (95% pure, 0.102 mol) of sodium cyanide were added. The resulting suspension was stirred magnetically and heated in an oil bath (bath temperature at 110 °C) for 45 min until all the gray selenium metal disappeared, and a colorless solution contaminated with a little bit of white solid was obtained. After cooling, this solution of NaSeCN in DMAC was used as described below.

Similarly, KSeCN in DMAC solution (pale yellow solution contaminated with a little bit of white solid) can be prepared by heating a mixture of potassium cyanide and gray selenium metal in DMAC at 110 °C for 12 h. The pure crystalline KSeCN may be obtained by cooling the DMAC solution at 0 °C.

Preparation of *o*-Nitrophenyl Selenocyanate. According to the procedure of Bauer[65a] *o*-nitroaniline (13.81 g, 0.10 mol), 39 mL of water, and 22 mL of concentrated hydrochloric acid are placed in a 250-mL two-neck flask equipped with a thermometer, a dropping funnel, and a magnetic stirrer.[65b] After the mixture was cooled to 2–3 °C in an ice–salt bath, a chilled solution of sodium nitrite (97% pure, 7.47 g, 0.105 mol) in 24 mL of water was added slowly maintaining the temperature at 2–3 °C. Stirring was then continued for 1 h at 2–3 °C. To this reaction mixture, 21 mL of chilled 25% aqueous sodium acetate solution was added dropwise until pH paper indicated a pH of about 4. The slightly brownish solution was filtered to remove traces of insoluble impurities and poured into a 1-L beaker surrounded by an ice–salt bath. The solution of NaSeCN (0.10 mol) in DMAC (see above) was cooled and then added dropwise to the reaction mixture in the beaker maintaining the temperature below 0 °C. The mixture was stirred with both a magnetic stirrer and a glass rod during the addition. The precipitated product was collected by filtration, washed with water, and dried to give 17.5 g of a dark yellow powder (mp 132–137 °C). This crude product was dissolved in 100 mL of chloroform and passed through a short plug of silica gel (40 g). Then 200 mL of chloroform was passed through the silica gel to ensure complete elution of the yellow *o*-nitrophenyl selenocyanate. Evaporation of the chloroform followed by recrystallization from acetone (120 mL) gave 11.37 g (50% yield) of orange-yellow crystals, mp 140–142 °C (lit.[65a] mp 142 °C). One gram of the crystals was recrystallized further from 20 mL of ethanol [the hot ethanol solution was treated with 40 mg of activated charcoal (Norit)] to give 0.91 g of yellow needles, mp 141.5–142.5 °C.

Preparation of Bis(*o*-nitrophenyl) Diselenide. The Source of the Seleninic Acid Catalyst 12. The *o*-nitrophenyl selenocyanate (10 g, 44 mmol) was added to a solution of 2.7 g (50 mmol) of sodium methoxide (Aldrich) in methanol (250 mL). The resulting light brown slurry was stirred under nitrogen for 3 h at room temperature. Water (200 mL) was added and the mixture was filtered. The solid was washed three times with water and dried to give 8.59 g (97%) of the diselenide as a light brown powder, mp 210–211 °C (lit.[61] mp 212–213 °C). It was this material which was used as the source of in situ generated, seleninic acid catalyst **22**.[62]

General Procedure for Olefin → Allylic Alcohol. Preparation of (*E*)-5-Octen-4-ol. To a magnetically stirred, ice-cooled solution of diphenyl diselenide (23.41 g, 75 mmol) in 250 mL of dry methylene chloride was slowly added 7.66 mL (8.50 g, 75 mmol) of chilled 30% hydrogen peroxide. After stirring vigorously for 30 min (white crystals deposit in 5–10 min), 12.5 g of powdered anhydrous magnesium sulfate was added and the mixture was stirred for an additional 30 min in the ice bath. The ice bath was removed, (*E*)-4-octene (5.61 g, 50 mmol) was added, and the mixture was stirred vigorously for 6 h at 24 °C. Chilled 90% *tert*-butyl hydroperoxide (30 mL, 268 mmol) was added to the reaction mixture which had been immersed in an ice bath; then, after removing the ice bath, the mixture was stirred for 20 h at 24 °C to give a pale orange solution with a lot of white precipitate. The white precipitate ($PhSeO_2H$ and hydrated $MgSO_4$) was filtered off (save for recovery of diphenyl diselenide) and washed with ether. The filtrate was concentrated (20 °C, aspirator) to give an oil. The oil was dissolved in 300 mL of ether and washed with 5% aqueous sodium carbonate (200 mL and then 100 mL, save), water (100 mL, save), 10% aqueous ferrous sulfate (200 mL and then 100 mL), water, saturated aqueous sodium hydrogen carbonate, water, and brine, successively. The ether extracts were dried over anhydrous magnesium sulfate. Concentration (20 °C, aspirator) gave an oil, which upon vacuum distillation gave 5.64 g (88%) of (*E*)-5-octen-4-ol, bp 58.5–59.5 °C (2.5 mm). NMR, IR, TLC, and GLC were identical with an authentic specimen.[15,16]

Following the same procedure (except that 20 h, instead of 6 h, was allowed for addition of "PhSeOH" to the olefin) (*Z*)-4-octene was converted to the same allylic alcohol [(*E*)-5-octen-4-ol] in 84% yield.

Preparation of Allylic Alcohol 9. In the case of citronellol methyl ether, the procedure was identical with that described for (*E*)-4-octene. The allylic alcohol **9** was obtained in 87% yield upon distillation, bp 76–77 °C (0.3 mm) [lit.[15,16] bp 77 °C (0.3 mm)]. NMR, IR, TLC, and GLC were identical with those for an authentic sample:[15,16] NMR ($CDCl_3$) δ 0.7–2.1 (m, 8 H, CH_2 and $CHCH_3$), 1.35 [s, 6 H, $C(CH_3)_2OH$], 3.35 (s, 3 H, OCH_3), 3.40 (t, 2 H, J = 6 Hz, OCH_2–), 5.65 (m, 2 H, =CH).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.86; H, 11.80.

Preparation of Allylic Alcohol 10. In the case of cyclooctene the same (except that 20 h, instead of 6 h, was allowed for addition of "PhSeOH" to the olefin) procedure as described in detail for (*E*)-4-octene was employed. The allylic alcohol **10** was obtained in 83% yield following distillation, bp 78–79 °C (3 mm) [lit.[66] bp 74 °C (2 mm)]; this product was spectrally and chromatographically identical with the authentic sample.[15,16]

Preparation of 1-Methyl-2-cyclohexenol (17). The procedure for preparation of the hydroxy selenide of 1-methyl-1-cyclohexene was identical (10 mmol of olefin) with that described above for (*E*)-5-octen-4-ol, and the hydroxyselenide **15** was isolated by chroma-

tography on 40 g of silica gel. Elution with 2:1 CH_2Cl_2–hexane gave 2.25 g of the hydroxy selenide **15**, which was dissolved in dichloroethane. Then 3.8 g of anhydrous chloramine-T[67] (Aldrich) was added and the mixture was refluxed for 2 h. The products were extracted with 100 mL of ether and the extracts were washed with 200 mL of 1 N sodium hydroxide solution, water, and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded an oil which was submitted to chromatography on silica gel. The epoxide byproduct was eluted with 5% ethyl acetate–hexane. Evaporation of the solvent gave 187 mg (16%) of 1,2-epoxy-1-methylcyclohexane, which was identified by comparison with an authentic sample. Further elution with 10% ethyl acetate–hexane followed by concentration gave an oil, which upon Kugelrohr distillation [80 °C (5 mm)] afforded 374 mg (33% based on olefin) of 1-methyl-2-cyclohexenol (**17**):[68] NMR (CCl_4) δ 1.20 (s, 3 H, CH_3), 1.5–2.2 (m, 6 H, CH_2), 2.72 (s, 1 H, OH), 5.59 (s, 2 H, olefinic).

Regeneration of Diselenide 2 by Reduction of the Reclaimed Seleninic Acid 1. In the foregoing description of the preparation of (*E*)-5-octen-4-ol it was noted that during the workup several of the washes (5% sodium carbonate washes and water washes) and a solid obtained by filtration were saved. This solid was added to the saved washes and 6 N hydrochloric acid was added to the resulting mixture until indicator paper revealed a pH of <3. Then 250 mL of a 10% sodium bisulfite solution was added which resulted in precipitation of a yellow solid (PhSeSePh). This suspension of diphenyl diselenide in water was extracted thrice with ether (300 mL, 100 mL, and finally 50 mL). In order to remove water and minor polar impurities, the combined ether extracts were passed quickly through a short plug of silica gel (50 g); then several small portions of ether were passed through the silica gel to ensure complete elution of the yellow diselenide. Evaporation of the ether afforded 21.9 g (93% recovery) of the diselenide **2**, mp 60.3–61.1 °C. This material was sufficiently pure for reuse. Recrystallization from hexane gave 19.42 g of yellow crystals, mp 60.8–61.8 °C; the mother liquid yielded a second crop (1.1 g, mp. 60.3–61.1 °C) of the diselenide.

Complications Resulting from Readdition of "PhSeOH" to the Allylic Alcohol Product. Formation of Diol Selenide 14. In the same manner as described above for preparation of (*E*)-5-octen-4-ol, 30% H_2O_2 (648 μL, 720 mg, 6.35 mmol) was added dropwise to a cooled and magnetically stirred solution of 1.98 g (6.35 mmol) of diphenyl diselenide in 22 mL of CH_2Cl_2. Powdered anhydrous magnesium sulfate (1.06 g) was then added and the mixture was stirred for an additional 30 min in the ice bath. (*E*)-4-Octene (475 mg, 4.23 mmol) was added and the suspension was stirred vigorously at room temperature for 15 h. The reaction mixture was cooled with an ice bath and any remaining anhydrous magnesium sulfate was hydrated by addition of 1.4 mL of water. Chilled 30% hydrogen peroxide (1.27 mL, 1.41 g, 12.5 mmol) was added dropwise, then the ice bath was removed and stirring was continued for 1 h at room temperature. The suspended solids were removed by filtration and washed with ether. The filtrate was concentrated to give an oil. The oil was dissolved in ether and washed with 5% aqueous sodium carbonate, water, and brine and dried ($MgSO_4$). Concentration afforded a solid which was recrystallized from hexane to give 608 mg (48%) of 4-phenylselenyl-3,5-dihydroxyoctane: mp 77.9–78.6 °C; NMR (90 MHz, $CDCl_3$) δ 3.28 (dd, 1 H, J_{AX} = 1.7 Hz J_{BX} = 4.3 Hz, CHSePh), 3.8–4.3 (m, 2 H, C*H*OH), 7.3–7.7 (m, 5 H, aromatic).

Anal. Calcd for $C_{14}H_{22}O_2Se$: C, 55.81; H, 7.36. Found: C, 56.00; H, 7.23.

Epoxidation of Cyclooctene. Data in Table II. To a cooled, stirred reaction mixture containing cyclooctene (110 mg, 1 mmol) and the selenium catalyst (0.05 mmol of the diaryl diselenide or 0.1 mmol of selenium dioxide) in 2 mL of methylene chloride was added 204 μL (227 mg, 2.0 mmol) or 220 μL (244 mg, 2.15 mmol) of chilled 30% hydrogen peroxide. When anhydrous magnesium sulfate was used, 250 mg was added after addition of the 30% hydrogen peroxide. The ice bath was allowed to melt (~30 min) and the reaction mixture was stirred for 16 or 20 h at room temperature. Small aliquots of the reaction mixtures were dissolved in ethyl acetate and washed with 10% aqueous sodium carbonate and brine in preparation for the gas chromatographic analysis performed (temperature programming from 100 to 200 °C) on a 6 ft × 0.125 in. glass column packed with 10% UCW-98 on 80/100 mesh Gas Chrom Q.

Epoxidation of Citronellol Methyl Ether. Data in Table III. To the mixture of 170 mg (1 mmol) of citronellol methyl ether and 0.005 mmol of bis(*o*-nitrophenyl) diselenide or bis(2,4-dinitrophenyl) diselenide[58] in 2 mL of methylene chloride, 204 μL (227 mg, 2.0 mmol) of chilled 30% hydrogen peroxide or 49 μL (69 mg, 2.0 mmol) of 98% hydrogen peroxide was added while stirring in an ice bath. When anhydrous magnesium sulfate was employed, 250 mg was added after addition of the 30% hydrogen peroxide. The ice bath was allowed to melt (~30 min) and stirring was continued at room temperature for 16 h. Aliquots of the reaction mixtures were prepared for GLC analyses as described above for the cyclooctene experiments. The GLC analyses were performed at 120 °C on a 6 ft × 0.125 in. glass column packed with 3% OV-17 on 80/100 mesh Gas Chrom Q.

Preparative Scale Epoxidations. Cyclooctene → Cyclooctene Epoxide. To a 250 mL round-bottom flask equipped with a mechanical stirrer and a reflux condenser were added 11.48 g of cyclooctene (Aldrich, 96% pure, equivalent to 11.02 g, 0.1 mol), 1.23 g (2.5 mmol) of bis(2,4-dinitrophenyl) diselenide, 25 g of anhydrous magnesium sulfate, and 100 mL of methylene chloride. The resulting suspension was cooled in an ice bath and 20.4 mL (22.67 g, 0.2 mol) of chilled 30% hydrogen peroxide was added dropwise (~5 min) while stirring vigorously. The ice bath was removed and after about 30 min the reaction mixture began to reflux. This spontaneous refluxing continued for about 1 h and then the mixture was stirred at room temperature for an additional 18.5 h. The hydrated magnesium sulfate was filtered off and washed with ether. This filtrate was diluted with 500 mL of ether and washed with water, 10% sodium carbonate, water, and brine and then dried ($MgSO_4$). Concentration gave an oil which was distilled by Kugelrohr [80 °C (0.1 mm)] to give 0.35 g as the first fraction and 11.99 g (95%) of cyclooctene oxide as the second fraction. NMR, IR, TLC, and GLC were identical with an authentic sample (Aldrich).

(*E*)-5-Decene → (*E*)-5,6-Epoxydecane. A 100-mL two-neck round-bottom flask equipped with a magnetic stirrer, a reflux condenser, and an ice cooling bath was charged with 25 mL of methylene chloride, 3.51 g (25 mmol) of (*E*)-5-decene, 2.51 mg (0.63 mmol) of bis(*o*-nitrophenyl) diselenide, and 6.25 g of powered anhydrous magnesium sulfate. To this vigorously stirred suspension was added dropwise 5.11 mL (5.67 g, 50 mmol) of chilled 30% hydrogen peroxide. The mixture was allowed to warm to room temperature and heated at reflux for 8 h. GLC analysis at this point revealed that olefin (~10%) still remained. The mixture was cooled in an ice bath and 3.3 g of anhydrous magnesium sulfate was added, followed by dropwise addition of 3.51 mL (3.90 g, 25 mmol) of chilled 30% hydrogen peroxide. The reaction mixture was then refluxed for 16 h, at which time GLC analysis revealed that no olefin remained.[69] [*This modified procedure employing heating, additional hydrogen peroxide, and a longer reaction time is recommended for less reactive olefins* which are not completely epoxidized under the milder conditions described above for preparation of cyclooctene epoxide.] Workup as described for epoxidation of cyclooctene afforded 4.2 g of a yellow oil which was distilled to give 3.9 g (90%) of (*E*)-5,6-epoxydecane, bp 39–40 °C (0.05 mm). It was identical in all respects with an authentic sample prepared by epoxidation of (*E*)-5-decene with *m*-chloroperbenzoic acid.

2-Methyl-2-heptene → 2,3-Epoxy-2-methylheptane. A reaction mixture consisting of 5.71 g (50 mmol) of 2-methyl-2-heptene, 50.3 mg (0.125 mmol) of bis(*o*-nitrophenyl) diselenide (**22**), and 12.5 g of anhydrous magnesium sulfate in 50 mL of methylene chloride was magnetically stirred vigorously; the 100-mL round-bottom flask was also equipped with a reflux condenser. This suspension was cooled in an ice bath and 10.22 mL (11.34 g, 0.1 mol) of chilled 30% hydrogen peroxide was added dropwise over about 3 min. Then the cooling bath was removed and after about 2.5 h the reaction mixture began to reflux spontaneously. Refluxing continued for about 1 h and then the suspension was stirred at room temperature for an additional 16.5 h. Workup as described above for epoxidation of cyclooctene gave an oil which upon kugelrohr distillation [80 °C (0.1 mm)] afforded 5.27 g (81%) of 2,3-epoxy-2-methylheptane. It was spectrally and chromatographically identical with an authentic sample prepared by epoxidation of 2-methyl-2-heptene with *m*-chloroperbenzoic acid.

Epoxidation of Allylic Alcohol 31. A reagent solution was prepared by addition of chilled 30% hydogen peroxide (204 μL, 227 mg, 2.0 mmol) to a mixture of 12.3 mg (0.025 mmol) of bis(2,4-dinitrophenyl) diselenide in 2 mL of methylene chloride. The resulting mixture was stirred for 1 h at room temperature. To this reagent was added 98 mg (1 mmol) of 2-cyclohexenol (**31**) and stirring was continued for 16 h at room temperature. At this point GLC analysis (6 ft × 0.125 in. glass column, 10% UCW-98 on 80/100 mesh Gas Chrom Q) revealed a 3:2 mixture of the *syn*- (**32**) and *anti*- (**33**) epoxy alcohols. Epoxy alcohols **32** and **33** were identified by comparison with authentic samples prepared by epoxidation of cyclohexenol **31** with *m*-chloroperbenzoic acid.[47,32d] The *syn*-epoxy alcohol **32** has the shorter GLC retention time.

Epoxidation of Allylic Alcohol 34. Epoxidation of **34** was carried out as described for epoxidation of **31** except that less catalyst [4.9 mg (0.01 mmol) of bis(2,4-dinitrophenyl) diselenide for 1 mmol of allylic

alcohol **34**] was used. GLC analysis at 150 °C (6 ft × 0.125 in. glass column, 10% OV-101 on Supelcon AW-DMCS) showed a 2:1 mixture of epoxy alcohols **35** and **36**. Epoxy alcohols **35** and **36** were identified by comparison with authentic samples prepared by epoxidation of **34** with *m*-chloroperbenzoic acid.[32a]

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Registry No.—**2,** 1666-13-3; **9,** 65252-78-0; **15,** 65252-79-1; **17,** 23758-27-2; *o*-nitrophenyl selenocyanate, 51694-22-5; PhSeOH, 5818-99-5; 4-phenylselenyl-3,5-dihydroxyoctane, 65252-80-4.

References and Notes

(1) Address correspondence to this author at the Department of Chemistry of Stanford University.
(2) As chance would have it, on the same day in which the experiments were performed which established that β-hydroxy selenides **3** resulted from reaction of olefins with solutions containing **1** and **2**, one of us (K.B.S.) learned in a phone conversation with Professor Hans Reich that he and his co-workers had also discovered this type of reactivity (see neighboring publication[3] in this issue).
(3) H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *J. Org. Chem.*, following paper in this issue.
(4) The addition process could just as well involve other selenium(II) electrophiles such as i and ii:

PhSeOSe(O)Ph PhSeOSePh
i ii

(5) G. Hölzle and W. Jenny, *Helv. Chim. Acta,* **41,** 593 (1958).
(6) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.,* **39,** 429 (1974).
(7) H. J. Reich, *J. Org. Chem.,* **39,** 428 (1974).
(8) D. L. J. Clive, *J. Chem. Soc., Chem. Commun.,* 100 (1974).
(9) (a) An intramolecular example of the addition of an arylselenenic acid to an olefin has been reported: H. J. Reich and J. E. Trend, *J. Org. Chem.,* **41,** 2503 (1976). (b) More recently it has been reported that reaction of cyclohexene with PhSeCN in THF–H_2O in the presence of a copper or nickel(II) halide gave *trans*-2-hydroxycyclohexyl phenyl selenide: A. Toshimitsu, S. Uemura, and M. Okano, *J. Chem. Soc., Chem. Commun.,* 166 (1977).
(10) In order to ensure complete reaction of the olefin we found it necessary to use 1.5 molar equiv of the diselenide **2** (i.e., enough diselenide to give rise to 3 molar equiv of "PhSeOH"). The disavantage of having to employ an excess of the selenium reagent is offset by the demonstration (see Experimental Section) that PhSeSePh (**2**) can be efficiently (>90%) recovered.
(11) The pK_a of phenylseleninic acid (**1**) is about 4.8 [J. D. McCullogh and E. S. Gould, *J. Am. Chem. Soc.,* **71,** 674 (1949)].
(12) (a) K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.,* **98,** 1986 (1976); (b) K. Akashi, R. E. Palermo, and K. B. Sharpless, *J. Org. Chem.,* in press.
(13) M. A. Umbreit and K. B. Sharpless, *J. Am. Chem. Soc.,* **99,** 5526 (1977).
(14) K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.,* 1979 (1973).
(15) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.,* **95,** 2697 (1973).
(16) R. F. Lauer, Ph.D. Thesis, Massachusetts Institute of Technology, 1974, p 102.
(17) Reich and co-workers have made some very interesting discoveries concerning the ability of selenium species to catalyze the dismutation of H_2O_2.[3]
(18) S. E. Dinizo, H. P. Jensen, R. F. Lauer, and K. B. Sharpless, unpublished results.
(19) However, decomposition pathways involving radical processes must also be considered. We have recently obtained evidence suggesting the involvement of radicals in the decomposition of allylic seleninyl peresters (M. A. Umbreit and K. B. Sharpless, unpublished results).
(20) (a) H. J. Reich, F. Chow and S. L. Peake, *Synthesis,* in press; (b) see also ref 3.
(21) P. A. Grieco, Y. Yokoyama, S. Gilman, and M. Nishizawa, *J. Org. Chem.,* **42,** 2035 (1977); T. Kametani, H. Nemoto, and K. Fukumoto, *Heterocycles,* **6,** 1365 (1977).
(22) R. F. Lauer, H. P. Jensen, and K. B. Sharpless, unpublished results.
(23) K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.,* **8A,** 9 (1975). A phase-transfer-catalyzed process for the oxidation/elimination of alkyl phenyl selenides utilizing chloramine-T was described. This same procedure was also reported to be effective for the generation of sulfilimines from sulfides. It was claimed that these were the first phase-transfer applications of chloramine-T. *This is wrong.* Oae and co-workers had much earlier reported the conversion of sulfides to sulfilimines with chloramine-T under phase-transfer conditions: K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Jpn.,* **42,** 2631 (1969). Carl R. Johnson (private communication) has found that chloramine-T is effective for the oxidation of sulfides to sulfilimines in the absence of an aqueous phase provided a phase-transfer catalyst is present (i.e., solid–liquid PTC).
(24) This is preferable to the earlier[23] procedure in that a phase-transfer catalyst, which can be difficult to separate from the desired products, is not necessary. However, we have found that secondary allylic alcohols are oxidized to α,β-unsaturated ketones under these conditions (T. Hori and K. B. Sharpless, unpublished results).
(25) The formation of epoxide is curious. To the best of our knowledge epoxide had not been observed as a byproduct in β-hydroxy selenoxide eliminations.
(26) D. N. Jones, D. Mundy, and R. D. Whitehouse, *Chem. Commun.,* 86 (1970).
(27) T. Hori and K. B. Sharpless, unpublished results.
(28) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Org. Chem.,* **39,** 2133 (1974).
(29) For an excellent review on oxidations employing organoselenium reagents see H. J. Reich, "Organoselenium Oxidations", in "Oxidation in Organic Chemistry", Part C, W. S. Trahanovsky, Ed., Academic Press, New York, N.Y., in press. This work includes a detailed critical evaluation of the problems associated with the various methods used for the oxidation/elimination of alkyl phenyl selenides.
(30) Phenylseleninic acid (**1**) has been reported to catalyze the decomposition of TBHP in refluxing benzene: D. T. Woodbridge, *J. Chem. Soc. B,* 50 (1966).
(31) TBHP (pK_a ~12–13) can be extracted from organic solutions with aqueous KOH, but in our experience this is not a very satisfactory method for its removal. Numerous alkaline washes are necessary and this can result in loss of water-soluble products. Emulsions were also a problem.
(32) (a) K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.,* **95,** 6136 (1973); (b) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *ibid.,* **96,** 5254 (1974).
(33) R. C. Michaelson, L. E. Khoo, and K. B. Sharpless, unpublished results.
(34) J. J. Pappas and W. P. Keaveney, *Tetrahedron Lett.,* 4273 (1966).
(35) M. A. P. Dankleff, R. Curci, J. O. Edwards, and H.-Y. Pyun, *J. Am. Chem. Soc.,* **90,** 3209 (1968).
(36) G. Sosnovsky and D. J. Rawlinson, "Chemistry of Hydroperoxides in the Presence of Metal Ions", in "Organic Peroxides", Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971.
(37) Further information on the safe handling and use of TBHP and other peroxides is available upon request from the Lucidol Division of the Pennwalt Corp., 1740 Military Rd., Buffalo, N.Y. 14240.
(38) D. Swern, J. T. Scanlan, and G. B. Dickel, "Organic Syntheses", Collect. Vol. **4,** Wiley, New York, N.Y., 1963, p 317.
(39) J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Radiochem.,* **6,** 279 (1974).
(40) (a) M. Mugdan and D. Young, *J. Chem. Soc.,* 2988 (1949); (b) G. B. Payne and P. H. Williams, *J. Org. Chem.,* **24,** 54 (1959); (c) H. C. Stevens and A. J. Kamens, *J. Am. Chem. Soc.,* **87,** 734 (1965); (d) C. G. Allan and A. N. Neogi, *J. Catal.,* **16,** 197 (1970).
(41) A. Guillemonat, *Ann. Chim. (Paris),* **11,** 143 (1939).
(42) (a) P. Sequin, *C. R. Acad. Sci.,* **216,** 667 (1943); (b) A. Stoll, A. Lindenmann, and E. Jucker, *Helv. Chim. Acta,* **36,** 268 (1953); (c) N. Sonoda and S. Tsutsumi, *Bull. Chem. Soc. Jpn.,* **38,** 958 (1965); (d) C. W. Wilson and P. E. Shaw, *J. Org. Chem.,* **38,** 1684 (1973).
(43) J. Itakura, H. Tanaka, and H. Ito, *Bull. Chem. Soc. Jpn.,* **42,** 1604–1608 (1969).
(44) Reich has also found that *o*-nitrophenylseleninic acid (**22**) is a very active catalyst.[20]
(45) The inhibition of the epoxidation process by coordinating and protic solvents is not surprising. Epoxidations by carboxylic peracids are well known to exhibit this same type of solvent sensitivity.
(46) Before adding the $MgSO_4$ the reactions are heterogenous (the presence of water droplets is apparent). To the extent that the arylseleninic acid catalyst is dissolved in these water droplets, the rate increase associated with addition of anhydrous $MgSO_4$ may be in part due to the increased catalyst concentration in the organic (CH_2Cl_2) phase caused by removal of the aqueous phase.
(47) H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.,* 1958 (1957).
(48) For an excellent review on the stereochemical aspects of epoxide synthesis, see G. Berti, *Top. Stereochem.,* **7** (1973).
(49) This conclusion is based on the reasonable assumption that the peracid **12a** has an approximately tetrahedral selenium center. A referee has pointed out that the epoxidizing species might be a hydrated peroxyseleninic acid [$ArSe(OH)_2OOH$] which, depending on the relative orientation of the substituents, may or may not be chiral at selenium. If one wishes to consider alternative structures for the active oxidant we feel that the cyclic peroxy species **12b** is a more likely candidate than the hydrate mentioned above. The only configurations of **12b** which are achiral at selenium are trigonal bipyramids with the peroxo unit equatorial and some combination of the aryl group, the lone pair, or the hydroxyl group in the two apical positions; such configurations would be highly disfavored by strain in the three-membered peroxo ring and by having at least one of the less electronegative substituents in the apical position.
(50) (a) D. R. Boyd, D. M. Jerina, and J. W. Daly, *J. Org. Chem.,* **35,** 3170 (1970); (b) F. Montari, I. Moretti, and G. Tane, *Chem. Commun.,* 135 (1969); (c) R. M. Bowman and M. F. Grundon, *J. Chem. Soc. C,* 2388 (1967); (d) D. R. Boyd and M. A. McKervey, *Q. Rev., Chem. Soc.,* **22,** 111 (1968); (e) J. Bjørgo, D. R. Boyd, R. M. Campbell, N. J. Thompson and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 2,* 606 (1976).
(51) T. Frejd and K. B. Sharpless, unpublished results.
(52) For successful asymmetric epoxidations of allylic alcohol **37,** see R. C. Michaelson, R. E. Palermo, and K. B. Sharpless, *J. Am. Chem. Soc.,* **99,** 1990 (1977).
(53) W. R. Adams, "Oxidation", Vol. 2, R. L. Augustine, Ed., Marcel Dekker, New York, N.Y., 1971, pp. 65–112.
(54) We have not tried to epoxidize tetrasubstituted olefins, but Reich has found[20a] that they are particularly good substrates for these seleninic acid

catalyzed epoxidations.
(55) K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40**, 947 (1975).
(56) J. D. McCullough and E. S. Gould, *J. Am. Chem. Soc.*, **71**, 674 (1949).
(57) (a) E. Rebane, *Ark. Kemi*, **26**, 345 (1966); (b) D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **93**, 197 (1973).
(58) (a) O. Foss and S. R. Svendsen, *Acta Chem. Scand.*, **8**, 1351 (1954); (b) E. Fromin and K. Martin, *Justus Liebigs Ann. Chem.*, **401**, 177 (1913).
(59) K. W. Rosenmund and H. Harms, *Ber.*, **53**, 2226 (1920).
(60) L. Chierici and R. Passerini, *Boll. Sci. Fac. Chim. Ind. Bologna*, **12**, 131 (1954); *Chem. Abstr.*, **49**, 6868c (1955).
(61) O. Behagel and H. Siebert, *Ber.*, **66**, 708 (1933).
(62) Since for the most electronegatively substituted cases the diselenide is prepared from the corresponding selenocyanate, it would be advantageous to be able to use the selenocyanate itself as the catalyst. This possibility was briefly explored in the case of the *o*-nitrophenyl selenocyanate. It was found that the selenocyanate was rather slow to be oxidized by hydrogen peroxide to the seleninic acid; this gave rise to induction periods when it was used as the catalyst. However, if the methylene chloride solution of the selenocyanate catalyst was first treated with an equivalent amount (e.g., if 5% catalyst then 5% Ph_3P) of triphenylphosphine, no induction period was observed and the results were identical with those using the corresponding diselenide as the catalyst.
(63) G. R. Waitkins and R. Shutt, *Inorg. Synth.*, **2**, 186 (1946).
(64) This procedure is based on earlier unpublished work by S. P. Singer in our laboratory; see also footnote 6 of ref 55.
(65) (a) H. Bauer, *Ber.*, **46**, 92 (1913); (b) P. A. S. Smith and J. H. Boyer, ref 38, p 75.
(66) A. C. Cope, M. R. Kinter, and R. J. Keller, *J. Am. Chem. Soc.*, **76**, 2757 (1954).
(67) (a) K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976); (b) K. B. Sharpless and S. P. Singer, *J. Org. Chem.*, **41**, 2504 (1976).
(68) E. N. Trachtenberg and J. R. Carver, *J. Org. Chem.*, **35**, 1646 (1970).
(69) Preliminary results (L. E. Khoo and K. B. Sharpless, unpublished) indicate that most of the seleninic acid catalyst **22** is still present and active at the end of these reactions. This is suggested by the observation that one can effect epoxidation of cyclooctene by adding cyclooctene and fresh hydrogen peroxide and anhydrous magnesium sulfate to a crude reaction mixture in which the epoxidation of (*E*)-5-decene has just been completed.

Syn Elimination of Alkyl Selenoxides. Side Reactions Involving Selenenic Acids. Structural and Solvent Effects on Rates[1]

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The olefin-forming syn elimination of alkyl aryl selenoxides was examined. The formation of β-hydroxy selenides by addition of the elements of benzeneselenenic acid (PhSeOH) to olefin product was found to be a persistent side reaction unless an alkylamine was present during syn elimination. The selenium(II) electrophile is provided by a comproportionation (reverse disproportionation) of Ph_2Se_2 and $PhSeO_2H$. If an intramolecular reaction is possible (as for the decomposition of **1**) only an unhindered secondary amine will prevent the electrophilic addition to the double bond. The selenoxide syn elimination was shown to be irreversible for compound **1**. Alkyl aryl selenoxides react with dimethyl acetylenedicarboxylate to form ylides (e.g. **8**). Solvent and substitutent effects on the rates of selenoxide syn eliminations were measured. Protic solvents reduce the rate of syn elimination. Chloro and phenyl substituents at either the α or β position or alkyl at the α position accelerate the syn elimination, whereas β-alkyl and methoxy substituents retard it. Methyl aryl selenoxides were shown to catalytically decompose hydrogen peroxide, a widely used oxidant for selenides. Reaction conditions for optimizing rates and yields for selenoxide syn eliminations are proposed.

The selenoxide syn elimination has been shown to be a mild and selective procedure for olefin formation.[3,4] The reaction frequently provides high yields of clean products, but side reactions have been identified in certain cases. For example, some α-phenylselenino ketones in acidic media undergo seleno-Pummerer reactions leading to α-dicarbonyl compounds.[3a] Reactions of enols, enolates, and enamines with active selenium(II) electrophiles formed during syn eliminations have also given unwanted products in some systems.[3a,5] Alkyl selenoxide eliminations, however, have generally been assumed to be free of byproducts, although low yields particularly for primary alkyl selenoxides have occasionally been reported in the published literature[4c,6] as well as in private communications to the authors. Modifications of the selenide reagent[6a] and elimination reaction conditions[3b] have been proposed to improve yields for such compounds.

The scattered results available suggested that selenoxide decompositions were complex. It is clear in retrospect that the long delay in recognition of the selenoxide syn elimination was a consequence of alternate reaction pathways available during the thermolysis.[7] The work described here was initiated to identify side reactions which may be occurring, and to gather product and kinetic data which will serve as a guide to optimizing reaction conditions for synthetic applications of the syn elimination.

Thermolysis of 2,2-Dimethyl-2,3-dihydrobenzo[*b*]-selenophene Oxide (1). The selenoxide is obtained by ozonization of 2,2-dimethyl-2,3-dihydrobenzo[*b*]selenophene in CH_2Cl_2, $CHCl_3$, or CF_2HCl at −78 to −60 °C. NMR spectra of the selenoxide can be obtained if taken rapidly at ambient probe temperature or more leisurely at sub-zero probe temperatures. Complete decomposition takes a few hours in organic solvents at room temperature. In the ^1H NMR spectrum of the ozonization solutions are observed two methyl singlets assigned to the diastereotopic *gem*-dimethyl group and an AB quartet corresponding to the benzylic hydrogens. An IR absorption assigned to the seleninyl $\nu_{Se=O}$ stretch[8] can be observed. Undecomposed solutions of **1** when treated with aqueous potassium iodide are reduced to the starting selenide. Although **1** does not lend itself to mass analysis, the above physical and spectral parameters satisfactorily characterize the compound.

If **1** is allowed to decompose completely, preparative TLC affords an ~4:1 mixture of isomeric alcohols in 77% combined yield which were assigned structures **2** (major) and **3** (minor) (Scheme I) on the basis of their NMR spectra and mass spectral analysis. The *p*-nitrobenzoate of **2** was isolated and successfully analyzed for C and H. The ^1H NMR spectrum of **2** in benzene-d_6 shows two AB quartets corresponding to the benzylic (δ 2.70, 2.96; J_{AB} = 15.2 Hz) and hydroxymethyl protons (δ 3.29, 3.25; J_{AB} = 11.0 Hz). Assignments are based on the magnitude of the benzylic coupling constant typical of indane structures[9] and the ~1 ppm downfield shift of the hydroxymethyl protons in going to the *p*-nitrobenzoate of **2**.

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