Concomitant Epoxide Deoxygenation and Deacetylation of Glycidyl Acetates Induced by Telluride Ion[1]

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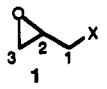
Received September 2, 1993•

Treatment of glycidyl acetates with telluride ion (Te^{2-}) produced by reduction of elemental Te with $LiEt_3BH$ yields allylic alcohols by loss of the epoxide oxygen atom and the acetyl group from the ester. If the glycidyl acetate is disubstituted at C-3, a rearrangement to an isomeric allylic alcohol competes with the deoxygenation–deacetylation. Triethylborane, a byproduct in the reduction of Te, is believed to play an important role as a Lewis acid since when it is absent or removed by addition of fluoride ion the reaction is extremely slow.

Introduction

The regiochemistry of nucleophilic additions to glycidyl derivatives (oxiranemethanols, e.g., 1) is an important



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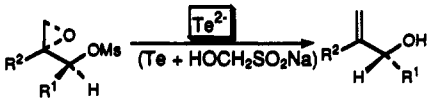
factor in planning syntheses with these reagents. The possible sites for attack by a nucleophile are C-1, C-2, or C-3. The choice of site is influenced both by steric and electronic factors in the glycidols as well as by the nature of the nucleophile and the reaction medium (solvent, presence of electrophiles, acidity, or basicity).[2]

In the reaction of telluride ion with glycidyl tosylates or mesylates, attack occurs at C-3 when that position is unsubstituted (eq 1) but at C-1 when C-3 is mono- or



(1)

(2)

disubstituted (eq 2).[3a] In aqueous medium the regiochemistry of the reaction of epoxycinnamyl tosylate (3-phenyloxiranemethanol tosylate) with telluride ion was mixed, but preferential C-1 attack was obtained by change of the medium to a less ionizing one which also necessitated a change in the reducing agent from rongalite ($HOCH_2SO_2Na$) to a boron hydride. The reactions exemplified by eqs 1 and 2 extend the usefulness of Sharpless–Katsuki asymmetric epoxidations (SAE) and kinetic resolutions (SKR).[3a]

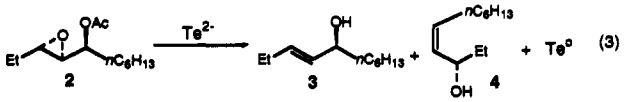
Two important observations were made for the reaction of telluride ion with a 1,3-disubstituted glycidyl tosylate: (1) the reaction was dependent on the reagent used to reduce Te^0, boron hydrides ($NaBH_4$, $LiEt_3BH$) but not rongalite being suitable, and (2) erythro isomers gave cis allylic alcohols while threo isomers gave trans allylic alcohols via a telluride-mediated 1,3-transposition process.[3] These results were attributed to the borane byproduct (e.g., BH_3 or Et_3B) from the reduction of tellurium, and the possible intervention of a boron–telluride species to account for the products from erythro and threo substrates.

Table 1. Yields and Product Distributions from 2 and Te° + Reducing Agent

reducing agent, condns	ratio 3/4	total yield, %
$NaBH_4$, DMF, 40 °C, 3 da	10	80
$LiEt_3BH$, THF, rt, 4 h	24	98
$LiEt_3BH$, THF, 0 °C, 24 h	32	98

Results

Changing the leaving group in a glycidyl derivative from a good one (mesylate or tosylate) to a relatively poor one (acetate) was thought to favor a change in telluride attack from C-1 to C-3. These glycidyl acetates were not very reactive when aqueous rongalite was used as the reductant for tellurium; long reaction times and low yields were the results. When lithium triethylborohydride was used, many, but not all, glycidyl acetates cleanly underwent deoxygenation of the epoxide function along with deacetylation of the acetate group. Chirality at C-1 is preserved as in 3 (eq 3). This deoxygenation is similar to that



(3)

observed when glycidols are treated with telluride ion obtained by reduction of the element with $LiEt_3BH$.[3a,b]

The transposition product, e.g., 4 (eq 3, Table 1), the main product from glycidyl tosylates,[3] is minor or absent in reactions of C-1, C-2, or C-3 monosubstituted derivatives and C-1, C-3, or C-1, C-2 disubstituted derivatives (eqs 3

• Abstract published in *Advance ACS Abstracts*, February 1, 1994.

(1) Taken in part from: Discordia, R. P. Ph.D. Thesis, Syracuse University, 1990. Zhang, Y. Ph.D. Thesis, Syracuse University, 1993.

(2) (a) For an extensive review of glycidol chemical see: Hanson, R. M. *Chem. Rev.* **1991**, *91*, 437–475. The hitherto somewhat confusing assignment of the *R*- or *S*-configurations to C-2 of glycidols is clarified, and we follow the recommended rule. (b) The factors influencing the direction of ring opening in epoxides have been cogently discussed: Behrens, C. H.; Sharpless, K. B. *Aldrichim. Acta* **1983**, *16*, 67–79. (c) For a discussion of synthetic applications of the stereo- and regioselective openings of glycidols see: Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589–604.

(3) (a) Dittmer, D. C.; Discordia, R. P.; Zhang, Y.; Murphy, C. K.; Kumar, A.; Pepito, A.; Wang, Y. *J. Org. Chem.* **1993**, *58*, 718–731. (The reactions reported in this paper involved stoichiometric amounts of tellurium. Recently, we have modified conditions to make the reactions catalytic in tellurium, the element being continuously reduced as it is formed in the reaction.) (b) Murphy, C. K. M.S. Thesis, Syracuse University, 1990.

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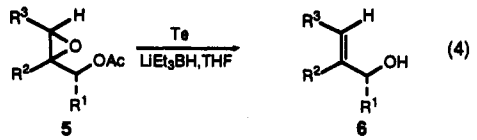
and 4). Yields of deoxygenated and deacetylated products (3, 6) are 70% or greater. As with 2, optically active glycidyl



(4)

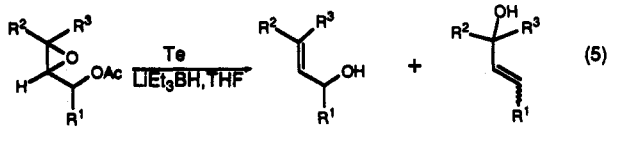
5 6

	R^1	R^2	R^3
a	Ph	H	H
b	H	Me	H
c	H	H	*n*-Pr
d	*n*-Bu	Me	H
e	*c*-C_6H_{11}	H	Me

acetates (*1S*)-**5a** and (*1S*)-**5d** gave allylic alcohols **6a** and **6d** with retention of configuration. (Compare the inversion of configuration obtained with the mesylate shown in eq 1). Elemental tellurium is recovered in all of the nucleophilic reduction[3] reactions. With **5a** there is some loss of optical activity in its synthesis via acetic anhydride that is possibly caused by the fact that the C-1 position is benzylic. Acetate ion may occasionally invert the configuration by backside attack on an ion pair. Formation of a free benzyl carbocation is expected to be inhibited by the electron-withdrawing inductive effect of the oxirane oxygen atom, although with better leaving groups the oxygen atom may be involved as a neighboring nucleophilic site.[4]

The reaction of diastereomeric mixtures of glycidyl acetates **5e** with Te–$LiEt_3BH$ resulted in complete conversion of the threo isomer and only partial conversion of the erythro isomer. The reaction of the threo isomer of **5e** was complete in 1 h at room temperature, while the erythro isomer had reacted only to the extent of 60% after 6 h.

Disubstitution at C-3 substantially changes the course of the reaction. Both deoxygenation (**8**) and rearrangement or transposition products (**9**) are obtained (eq 5), the



(5)

7 8 9

	R^1	R^2	R^3
a	H	$Me_2C{=}CHCH_2CH_2$	CH_3
b	*n*-C_6H_{13}	CH_3	CH_3

latter being the major. Treatment of racemic epoxygeranyl acetate (**7a**) with Te–$LiEt_3BH$ either at room temperature or at 0 °C for about 5 h gave a mixture of geraniol (**8a**) (6%, a mixture of cis and trans isomers) and the rearranged product linalool (**9a**) (62%).

If the same reaction is conducted in the presence of tetra-*n*-butylammonium fluoride, 80% of the starting epoxy acetate, **7a**, is recovered after 50 h at room temperature; only 5% of linalool, **9a**, is obtained. If basic rongalite is used as the reducing agent for tellurium, **8a** (2%), **9a** (34%), and epoxygeraniol (12%), the hydrolysis product, were obtained after 30 h at room temperature. Treatment of racemic **7b** (a nearly equimolar mixture of erythro and threo isomers obtained by epoxidation with *tert*-butyl hydroperoxide (TBHP) and $VO(acac)_2$[5]) with Te^0–$LiEt_3BH$ gave results similar to those obtained with **7a** although the reaction time had to be extended to 12 h. The rearrangement product **9b** (42%) was obtained as a mixture of *E* and *Z* isomers which is analogous to the results with glycidyl sulfonate esters which give the *E* isomer from the threo and the *Z* isomer from the erythro glycidyl derivatives.[3a] Deoxygenated product **8b** (24%) and unreacted glycidyl acetate **7b** (34%) also were obtained. Optically active (*1S,2S*)-*erythro*-**7b**, prepared in 45% yield from the glycidol (>95% ee) obtained by a Sharpless kinetic resolution,[6] gives both **8b** (with retention of configuration) and (*Z*)-**9b**.

Discussion

Discussion will focus on the following: (1) the Lewis acid (borane or Li^+) effect as it relates to glycidyl acetates and to the regioselectivity of the telluride reaction, (2) the reactivity difference between *erythro* and *threo* secondary glycidyl acetates, (3) the change in behavior of the reaction of glycidyl acetates upon disubstitution at C-3, (4) the potential usefulness of the telluride deoxygenation in deblocking an allylic double bond that is protected as an epoxide in allylic acetates.

Borohydride reducing agents for tellurium are important in achieving the results shown in eqs 3–5. The reduction of tellurium presumably forms borane byproducts (eq 6)

$$2LiEt_3BH + Te \rightarrow Li_2Te + 2Et_3B + H_2 \qquad (6)$$

$$Et_3B + n\text{-}Bu_4N^+F^- \rightarrow (Et_3BF)^-n\text{-}Bu_4N^+ \qquad (7)$$

which, perhaps with lithium ions, catalyze these reactions; and boranes have been implicated in our previous work.[3a] That lithium ions are not essential is shown by the fact that the same reactions may be performed with $NaBH_4$ in DMF. Inactivation of the borane by complexation with fluoride ion (eq 7) blocks the reaction as shown by the behavior of epoxygeranyl acetate, **7a**, in the presence of $n\text{-}Bu_4N^+F^-$. Previously, the transposition reaction of a *threo*-epoxy tosylate was shown to be slow in the absence of boranes but enhanced by addition of triethylborane.[3a] Fluoride ions also inhibited borane-catalyzed side reactions of telluride ion with epoxycinnamyl tosylate.[3a] One can therefore infer that the borane plays a catalytic role probably by complexation with an oxygen atom of the epoxide or the acetate.[7]

Deoxygenation of glycidyl acetates **2** and **5a–e** can be attributed to rate-determining attack of telluride ion at C-3 rather than at C-1. The phenomenon of nucleophiles attacking principally at C-3 in reactions of glycidyl derivatives catalyzed by Lewis acids is fairly general[2,8] except in those glycidols which react at C-1 following a

(4) Francl, M. M.; Hansell, G.; Patel, B. P., Swindell, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 3535–3539.

(5) Threo and erythro specificity in epoxidations has been discussed: Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63–74.

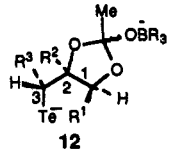
(6) SKR usually gives mainly the erythro isomer: Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237–6240.

(7) The addition of boron Lewis acids (e.g., Et_3B) significantly increases the rates of reduction of esters and epoxides by $LiBH_4$. Complexation of the borane to an oxygen functionality was suggested. (a) Brown, H. C.; Narasimhan, S. *J. Org. Chem.* **1984**, *49*, 3891–3898. (b) Yoon, N. M.; Oh, I. H.; Choi, K. I.; Lee, H. J. *Heterocycles* **1984**, *22*, 39–42.

Payne rearrangement.[9] With glycidol itself, the preference for nucleophilic attack on mesylate and tosylate derivatives is at C-1 except when a Lewis acid is present.[8f] The regiochemistry of opening of epoxides has been interpreted on the basis of hard–soft acid–base theory; Lewis acid catalysis favors attack at a secondary over a primary carbon atom of an epoxide and is the predominant "pulling" factor in ring openings even with soft nucleophiles.[10]

Attack of telluride ion at C-3 can lead to formation of a relatively strain-free five-membered 1,3-dioxolane intermediate (**10**, Figure 1) from the strained three-membered epoxide. Attack at C-1 initially would leave the epoxide ring intact (**11**, Figure 1). A composite of transition states for these two processes is represented in Figure 1 in which a (1*R*)-configuration is shown. An epitelluride intermediate (not shown) may be involved following initial attack of telluride ion.[3a] The involvement of an epoxide oxygen atom in intramolecular attack at a proximate electrophilic site is analogous to the solvolysis reactions of glycidyl 3,5-dinitrobenzoates which proceed through a 1-oxabicyclobutonium ion[4] and to attack by the epoxide oxygen atom on the carbonyl group of glycidol esters initiated by nucleophilic ring opening of the epoxide[11] (cf. Figure 1). Lewis acid complexation at the carbonyl oxygen atom in preference to the epoxide oxygen is expected from consideration of proton affinities.[12] Alternative mechanisms for reactions of both glycidyl tosylates[3a] and glycidyl acetates involving successive one-electron transfers from telluride ion were considered less plausible because these processes, with their radical and anionic intermediates, could give variable stereochemistry.

The diminished reactivity of erythro isomers as compared to threo isomers may be caused by unfavorable steric interactions of R^1 with C-3 in the dioxolane intermediate **12**.



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Direct attack of telluride ion at C-2 is hindered if R^2 is alkyl; if R^2 = H, the intermediate **13** from such an attack would be expected to give two isomeric products in comparable amounts via paths *a* and *b*, instead of the single products, **3** and **6a–e**, obtained almost exclusively. In glycidyl acetates shown in eqs 3 and 4, the electron-withdrawing inductive effect of the acetoxy group is

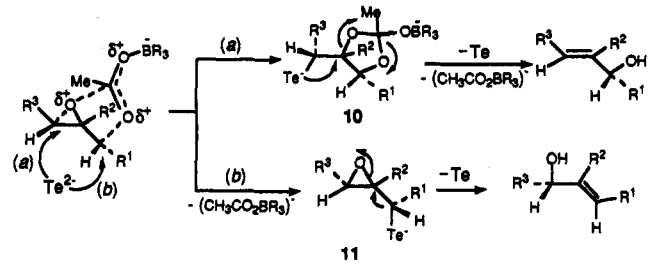
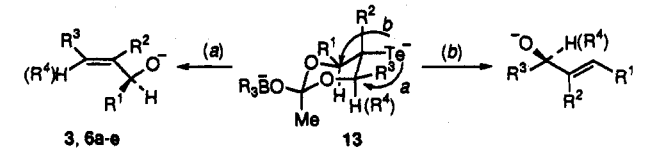


Figure 1. The boron-catalyzed reaction of a threo glycidyl acetate is facilitated by path *a* because strain is relieved by conversion of the epoxide to a 1,3-dioxolane intermediate.

expected to disfavor attack at C-2.[13] C-2 attack is favored in several cases,[14] such as when electron-withdrawing (electronegative) substituents are on both C-1 and C-3.[2c]



Because Te^{2-} is a large ion (ionic diameter 4.22 Å) and may be encumbered with additional tellurium as in Te_n^{2-},[15] it could conceivably collide with two adjacent carbon atoms of glycidyl derivatives more or less simultaneously, with appropriate orbitals of the tellurium species overlapping with two carbon–oxygen σ^* orbitals.

With 3,3-disubstituted compounds **7a** and **7b** (eq 5) the attraction of Te^{2-} for the expected greater positive charge on C-3 is offset by steric hindrance so that telluride attack also occurs at C-1 or C-2 or perhaps both together. The two products, **8** and **9**, could be derived from attack at C-2 via **13**, but attack at C-1 and C-3 also explains the results. The ratios of **8a** to **9a** and **8b** to **9b** are approximately 1:11 and 1:2, respectively, and correlate with the steric hindrance at C-3 and C-1. When C-1 is unsubstituted and the substituents at C-3 are more bulky as in **7a** (**13**, R^1 = H, R^3 = $Me_2C{=}CHCH_2CH_2$, R^4 = Me) compared with **7b** (**13**, R^1 = n-C_6H_{13}, R^3 = R^4 = Me), attack of Te^{2-} at C-1 to give **9a** is favored to a greater degree. It is difficult to differentiate between direct displacement on C-1 or C-3 and indirect displacements via a prior displacement on C-2 to give intermediate **13**. With **7a** it is unreasonable on steric grounds to suppose that attack at the secondary epoxide carbon atom C-2 would be preferred over attack at the primary acetate carbon atom C-1. To imagine that the telluride ion in **13** would show such little discrimination between a tertiary carbon atom (C-3) and a secondary carbon atom (C-1) of **7b** is also unreasonable, given the 1:2 ratio of **8b**:**9b**. Finally, in cases where C-2 attack is sterically feasible because of substitution at C-1 and C-3 (as in **2** and **5e** where all three carbon atoms are secondary), the reaction proceeds to give predominantly one product (**3**, **6e**, respectively) rather than the two expected from the decomposition of **13**.

The epoxide functionality has been put forth as an alkene protecting or blocking group provided that methods for

(8) (a) McClure, D. E.; Arison, B. H.; Baldwin, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 3666–3668. (b) Caron, M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1557–1560. (c) Kirshenbaum, K. S.; Sharpless, K. B. *Chem. Lett.* **1987**, 11–14. (d) Takahashi, K.; Ogata, M. *J. Org. Chem.* **1987**, *52*, 1877–1880. (e) Onaka, M.; Sugita, K.; Takeuchi, H.; Izumi, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1173–1174. (f) Klunder, J. M.; Onami, T.; Sharpless, K. B. *J. Org. Chem.* **1989**, *54*, 1295–1304. (g) Chini, M.; Crotti, P.; Flippin, L. A.; Gardelli, C.; Giovani, E.; Macchia, F., Pineschi, M. *J. Org. Chem.* **1993**, *58*, 1221–1227.

(9) Behrens, C. H.; Soo, Y. K.; Sharpless, K. B.; Walker, F. J. *J. Org. Chem.* **1985**, *50*, 5687–5696.

(10) Kayser, M. M.; Morand, P. *Can. J. Chem.* **1980**, *58*, 302–306.

(11) Lok, C. M. *Chem. Phys. Lipids* **1978**, *22*, 323–337.

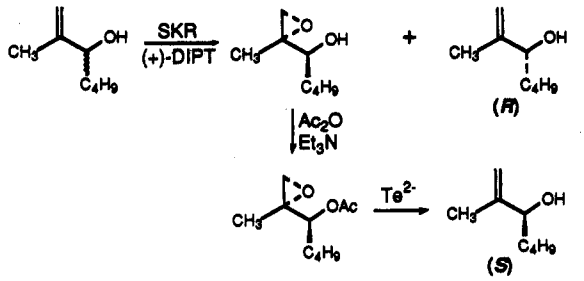
(12) The proton affinity of the carbonyl oxygen atom in ethyl acetate (200.7 kcal mol^{-1}) is greater than that of the oxygen atom in 2-methyloxirane (194.7 kcal mol^{-1}) or in oxirane itself (187.9 k cal mol^{-1}): Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. No. 1.

(13) (a) Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw Hill: New York, 1962; pp 16–17, 124. (b) Chong, J. M. *Tetrahedron Lett.* **1992**, *33*, 33–36.

(14) Colvin, E. W.; Robertson, A. D.; Wakharkar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 312–314.

(15) The telluride species produced in the reduction are more accurately described as Li_2Te_n (n = 1, 2, ...): Björgvinsson, M.; Schrobilgen, G. J. *Inorg. Chem.* **1991**, *30*, 2540–2547. The formation of Et_2BTeLi also may occur: $LiEt_3BH + Te \rightarrow Et_2BTeLi + C_2H_6$.

Scheme 1



easy deoxygenation are available.[16] A number of reagents perform such a function.[17] Tellurium reagents that have been used are *O,O*-diethyl phosphorotelluroates (room temperature, 17–42 h)[18] and sodium hydrogen telluride (refluxing ethanol, treatment of the β-hydroxytellurol with *p*-toluenesulfonyl chloride and pyridine).[19] We reported earlier on the telluride-induced transformation of glycidyl tosylates to allylic alcohols.[3a] The use of Te–$LiEt_3BH$ to deoxygenate epoxides with retention of the alkene geometry is limited so far to glycidyl acetates and in particular to those that are not disubstituted at C-3. For the deblocking of an epoxidized double bond of suitable allylic acetates, the method is convenient and mild. The tellurium is not wasted; it is recovered and can be reused. Catalytic methods in which the tellurium is reduced as it is formed are feasible (see note to ref 3a). The reactions are complete at room temperature in about 20 min for C-2 or C-3 monosubstituted allylic alcohols and in 2–6 h for more highly substituted systems. Care should be taken that all of the lithium triethylborohydride is consumed in the reduction of tellurium if functional groups capable of reaction with the borohydride are present. The triethylborane byproduct apparently is essential for the reaction, but it also may react with other functionalities.

The C-1 substituted allylic alcohols that are obtained from glycidyl acetates and Te^{2-} are opposite in configuration to those of the allylic alcohols resulting from a kinetic resolution (SKR). As exemplified in Scheme 1, the deoxygenation of the glycidol acetate enables a complete resolution of an allylic alcohol to be accomplished. This will be practical only for those allylic alcohols whose enantiofacial selectivity (k_{rel}) in the Sharpless kinetic resolution process is high so that one obtains 50% of pure glycidol of one configuration at the carbinol carbon atom and 50% of allylic alcohol of the opposite configuration.

Experimental Section

^{13}C and ^1H NMR spectra were taken at 75 and 300 MHz, respectively, in $CDCl_3$ unless otherwise specified. *J* values are given in Hz. Optical rotations were obtained by means of a Perkin-Elmer 241 polarimeter. Reactions were monitored by TLC on silica gel (250 μm) and visualized by ultraviolet light, phosphomolybdic acid, I_2, or anisaldehyde. Melting points were obtained either on a hot stage apparatus or in a Pyrex capillary (uncorrected). Enantiomeric excesses of secondary alcohols were determined by ^1H NMR spectroscopy of esters of (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA or Mosher reagent).[20] An ee > 95% signifies that no absorption caused by the presence of the other enantiomer could be observed. MTPA esters of racemic alcohols were used on occasion to identify the chemical shifts of diastereotopic protons. Benzene-d_6 solvent often gives better resolution of these protons than does $CDCl_3$.

Unless otherwise noted, materials were obtained from commercial sources and used without further purification. Rongalite (sodium hydroxymethanesulfinate dihydrate) was stored in a freezer. THF was distilled from sodium/benzophenone, and hexanes were fractionally distilled. Methylene chloride was distilled if it had been stabilized with methanol and should not be stored over sieves.[21] Ether was distilled from lithium aluminum hydride. DMF was purified by drying with calcium hydride and distillation from barium oxide. Pyridine and triethylamine were distilled before use. All reagents used in the Sharpless asymmetric epoxidations were purified as previously described.[21] (*R*)-(+)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPACl) was prepared from the acid by treatment with oxalyl chloride in hexanes with a few drops of DMF, and MTPA esters were prepared as described previously.[21] Epoxidations with *m*-CPBA[3a] and TBHP-$VO(acac)_2$[5,22] and the Sharpless asymmetric epoxidations and kinetic resolutions[3,21] were performed as described previously. Acetate esters were prepared by treatment of the glycidol (1.0 equiv) with acetic anhydride (1.2 equiv), triethylamine, and (*N,N*-dimethylamino)pyridine (DMAP) (2% molar equiv) in CH_2Cl_2 (0.25 M in glycidol) at room temperature. Workup entails addition of water, extraction with CH_2Cl_2 (2–3 × 20 mL), drying, and removal of solvent. The product may be purified by flash chromatography on silica gel (hexane–ether).

General Procedure for Telluride Reactions with Glycidol Acetates. Elemental Te (~200-mesh gray powder, 1.2 equiv based on the glycidyl acetate) is reduced by lithium triethylborohydride (Super-Hydride, 1.0 M solution in THF, 2.4 equiv) under an inert atmosphere (N_2 or Ar) at room temperature for about 1 h.[3a,23] Alternatively, the tellurium may be reduced with $NaBH_4$ in DMF.[3a,24] It is presumed that the BH_3-Me_2NH complex (formed via DMF and BH_3[25] in the reduction of Te) catalyzes the telluride reaction analogously to triethylborane. The glycidyl acetate in THF (0.5 M in acetate) was added slowly via syringe to the pink, chalky lithium telluride. The reaction was monitored by the color change and by TLC. For C-3 and C-2 monosubstituted primary acetates the reaction time is 20 min; secondary acetates take 2–6 h. Both primary and secondary acetates disubstituted at C-3 react slowly over a period of several days. When the reaction is complete, air is passed through the mixture for 20–30 min to ensure a complete conversion of Te^{-2} to Te^0. The black precipitate of elemental tellurium was filtered through a pad of Celite. The filtrate was dried ($MgSO_4$), and concentrated on a rotary evaporator to give a crude product, which can be purified by vacuum distillation or by column chromatography.

Treatment of (αS,2R,3S)-3-Ethyl-α-*n*-hexyloxiranemethanol Acetate (2) with Telluride Ion. (±)-(*E*)-3-Undecen-5-ol [prepared from (*E*)-2-pentenal and *n*-hexyl magnesium bromide][26] was subjected to a Sharpless kinetic resolution (SKR) [(+)-diisopropyltartrate (DIPT)] analogously to the (*Z*)-allylic alcohol[6,26] to give *erythro*-(α*S*,2*R*,3*S*)-3-ethyl-α-*n*-hexyloxiranemethanol [$[\alpha]^{25}_D$ −3.45° (*c* 4.46, $CHCl_3$), > 95% ee by NMR of MTPA ester]. The oxiranemethanol (0.400 g, 2.15 mmol) was converted to the acetate, obtained as a colorless oil with a fruity odor (0.404 g, 1.77 mmol, 82%): $[\alpha]^{25}_D$ −42.7° (*c* 4.86, $CHCl_3$); ^1H NMR δ 0.85 (t, 3, *J* = 6.9), 0.95 (t, 3, *J* = 7.5), 1.10–1.17 (m, 12), 2.03 (s, 3), 2.68 (AB q, 1, *J* = 2.1), 2.87 (AB sextet, 1, *J* = 2.1, 5.7), 4.67 (AB q, 1, *J* = 6.0); ^{13}C NMR δ 9.68, 13.97, 20.93, 22.48, 24.68, 24.82, 29.02, 31.30, 31.59, 58.18, 58.24, 72.91, 170.27; IR (neat) 1743 (s), 1236 (s) cm^{-1}. (−)-Acetate **2** (0.15 g, 0.658

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mmol) was treated at 40 °C with sodium telluride (1.00 mmol, 1.5 molar equiv), prepared by reduction of elemental Te with $NaBH_4$ in DMF. (−)-(*S*)-(*E*)-3-Undecen-5-ol (**3**) (0.0928 g, 0.546 mmol, 83%, >95% ee via ^1H NMR of MTPA ester) was obtained as an oil: $[\alpha]^{25}_D$ −3.62° (*c* 1.93, $CHCl_3$) [lit.[26] $[\alpha]^{25}_D$ −3.86° (*c* 2.46, $CHCl_3$)]. (*R*)-MTPA ester of (±)-(*E*)-3-undecen-5-ol: ^1H NMR δ 3.55 (s, 3), 3.56 (s, 3), 5.25–5.50 (br m, 4), 5.75–5.95 (br m, 2). (*R*)-MTPA ester of (−)-(*S*)-(*E*)-3-undecen-5-ol: ^1H NMR δ 3.55 (s, 3), 5.25–5.48 (br m, 2), 5.75–5.88 (m, 1). (*R*)-MTPA ester of (+)-(*R*)-(*E*)-3-undecen-5-ol: ^1H NMR δ 3.56 (s, 3), 5.40–5.50 (m, 2), 5.85–5.95 (m, 1). A similar reaction in which acetate **2** (0.150 g, 0.658 mmol) was treated at room temperature with telluride ion prepared by reduction of Te with $LiEt_3BH$ in THF also gave (−)-(*S*)-(*E*)-3-undecen-5-ol (**3**) in somewhat better yield (0.110 g, 0.647 mmol, 98%, >95% ee): $[\alpha]^{25}_D$ −3.60 (*c* 1.02, $CHCl_3$). ^1H NMR analysis indicated the presence of a small amount of (+)-(*S*)-(*Z*)-4-undecen-3-ol (**4**) (ratio of major to minor product, 24:1) that was purified by flash chromatography (1:10 ether/hexanes) to give the colorless (+)-(*S*)-(*Z*)-isomer (0.003 g, 0.018 mmol 2.7% >95% ee): $[\alpha]^{25}_D$ +15.1° (*c* 0.20, $CHCl_3$), [(−)-(*R*)-(*Z*)-4-undecen-3-ol, lit.[6] $[\alpha]^{24}_D$ −17.0° (*c* 12.6, EtOH), lit.[26] $[\alpha]^{24}_D$ −20.3° (*c* 1.3, EtOH)]. When the reaction of acetate **2** (0.15 g, 0.658 mmol) was performed at 0 °C (24 h) with Te–$LiEt_3BH$, the same two products were obtained in a ratio of 32:1 as indicated by ^1H NMR of the crude product. The ratio of isolated products was somewhat less: (−)-(*S*)-(*E*)-3-undecen-5-ol (0.107 g, 0.629 mmol, 96%, >95% ee), $[\alpha]^{25}_D$ −3.66° (*c* 1.11, $CHCl_3$), and (+)-(*S*)-(*Z*)-4-undecen-3-ol (0.0029 g, 0.018 mmol, 2.7%), $[\alpha]^{25}_D$ +15.0° (*c* 0.19, $CHCl_3$).

(αS,2S)-α-Phenyloxiranemethanol. TBHP (7.5 mmol, 1.36 mL of 5.5 M solution in isooctane) was added to (*R*)-phenylvinyl carbinol[28a] (0.67 g, 5.0 mmol, 94% ee, $[\alpha]$ +8.17°, *c* 2.62, C_6H_6) and $VO(acac)_2$ (0.026 g, 0.100 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was stirred for 6.5 days. Saturated aqueous sodium sulfite (5 mL) was added to quench the excess TBHP. The aqueous layer was extracted with ether (2 × 5 mL), and the combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated to give a light brown oil, which was purified on silica gel with hexanes/ether (5:1). The (αS,2S) isomer was predominant and was obtained as a nearly colorless oil (0.58 g, 3.9 mmol, 77%): $[\alpha]^{23}_D$ +87.5° (*c* 2.3, $CHCl_3$) [lit.[27] $[\alpha]^{23}_D$ −100.2° (*c* 2.31, $CHCl_3$) for (αR,2R)-isomer]; ^1H NMR δ 2.32–2.41 (br s, 1), 2.75–2.80 (m, 1), 2.96-3.00 (m, 1), 3.22–3.28 (m, 1), 4.91–4.97 (d, 1, *J* = 1.8), 7.31–7.45 (m, 5).

α-Phenyloxiranemethanol Acetate (5a). The epoxy alcohol (0.57 g, 3.8 mmol) in CH_2Cl_2 (20 mL) was converted to the acetate which was purified by chromatography on silica gel with hexane/ether (6:1) to give a light yellow oil (0.48 g, 2.5 mmol, 66%), the proton NMR of which indicated a 5:1 ratio of erythro/threo isomers: ^1H NMR erythro isomer δ 2.1 (s, 3), 2.65–2.70 (m, 1), 2.78–2.81 (m, 1), 3.25–3.29 (m, 1), 5.86–5.88 (d, 1, *J* = 6.0), 7.32–7.40 (m, 5); threo isomer δ 2.3 (s, 3), 2.68–2.72 (m, 1), 2.80–2.83 (m, 1), 3.31–3.35 (m, 1), 5.49–5.52 (d 1, *J* = 6.9), 7.32–7.40 (m, 5); ^{13}C NMR δ 21.03, 44.79, 52.79, 73.89, 127.35, 128.52, 128.67, 136.03, 169.83. Small absorptions for the three carbon atoms of the threo glycidyl system are observed at *ca.* δ 45.0, 53.0, 76.7.

Treatment of α-Phenyloxiranemethanol Acetate (5a) with Telluride Ion. Tellurium (0.38 g, 3.0 mmol) was reduced by $LiEt_3BH$ (6.0 mmol, 6.0 mL of 1.0 M solution in THF) at room temperature under argon. The acetate (0.470 g, 2.48 mmol) in THF (2 mL) was added to the purple solution. Workup was according to the general procedure. The crude yellow (1*R*)-1-phenyl-2-propen-1-ol (**6a**) was purified by flash chromatography [hexanes/ether (5:1)] to yield a colorless oil (0.22 g, 1.6 mmol, 65%): $[\alpha]^{23}_D$ +8.19° (*c* 2.60, C_6H_6) [lit.[3] $[\alpha]^{23}_D$ +8.35° (*c* 3.58, C_6H_6)], 93% ee via ^1H NMR of MTPA ester. Spectral data are consistent with those of authentic 1-phenyl-2-propen-1-ol.

(±)-2-Methyl-2,3-oxiranemethanol.[28] Epoxidation of 2-methyl-2-propen-1-ol (1.44 g, 20 mmol) with *m*-CPBA (4.14 g, 24 mmol) followed by removal of CH_2Cl_2 by distillation gave a semisolid residue which was purified by further distillation (23 °C, 1.8 mm) to give the glycidol (0.88 g, 9.1 mmol, 45%): ^1H NMR δ 1.31 (s, 3), 2.01 (br s, 1), 2.60–2.61 (d, 1, *J* = 4.7), 2.84–2.86 (d, 1, *J* = 4.7), 3.51–3.56 (d, 1, *J* = 12.4), 3.65–3.69 (d, 1, *J* = 12.4); ^{13}C NMR δ 17.9, 51.0, 57.4, 64.2; IR (thin film) 3419 (s), 2972 (m), 2875 (w), 1456 (m), 1206 (m), 1047 (s) cm^{-1}.

(±)-2-Methyl-2,3-oxiranemethanol Acetate (5b). The epoxy alcohol (0.88 g, 9.1 mmol) was converted to the acetate in the usual manner. The crude product (1.08 g) was distilled (Kugelrohr) to give a colorless oil (0.64 g, 5.3 mmol, 59%): bp 36–38 °C (0.65 mm); ^1H NMR δ 1.33 (s, 3), 2.06 (s, 3 H), 2.63–2.65 (d, 1, *J* = 4.7), 2.73–2.75 (d, 1, *J* = 4.7), 3.90–3.94 (d, 1, *J* = 12.0), 4.19–4.23 (d, 1, *J* = 11.9); ^{13}C NMR δ 19.5, 45.5, 52.3, 58.0, 67.1, 170.2.

Treatment of 5b with Telluride Ion. The epoxy acetate **5b** (0.45 g, 3.7 mmol) was added to tellurium (0.57 g, 4.4 mmol) reduced with $LiEt_3BH$ (8.8 mL of 1.0 M solution in THF, 8.8 mmol). A black precipitate of elemental tellurium was formed during the addition. Thin-layer chromatography showed that the reaction was complete in 10 min. Workup was as usual except that the solvents were removed by simple distillation to give crude 2-methyl-2-propen-1-ol (**6b**, 0.21 g) contaminated with solvent. Further purification was accomplished by distillation (9.8 mm) at room temperature to afford a clear oil (0.19 g, 2.6 mmol, 70%): ^1H NMR δ 1.67 (s, 3), 2.40–2.85 (br s, 1), 3.99 (s, 2), 4.82 (s, 1), 4.94 (s, 1); ^{13}C NMR δ 19.1, 66.6, 109.7, 144.9. The proton NMR data were identical with those reported previously.[29]

(±)-(*E*)-3-Propyloxiranemethanol.[30] The product from (*E*)-2-hexen-1-ol (3.4 g, 33 mmol), $VO(acac)_2$ (0.43 g, 1.6 mmol), and TBHP (9.6 mL of 4.1 M solution, 39 mmol) was purified by flash chromatography (hexanes/ether (3:1)) to give a colorless oil (3.13 g, 27.0 mmol, 82%): ^1H NMR δ 0.91–0.95 (t, 3, *J* = 7.3), 1.39–1.56 (br m, 4), 2.49 (br s, 1), 2.88–2.95 (m, 2), 3.54–3.60 (dd, 1, *J* = 4.4, 8.1), 3.85–3.90 (dd, 1, *J* = 2.2, 10.2); ^{13}C NMR δ 13.8, 19.2, 33.5, 55.8, 58.5, 61.7.

(±)-(*E*)-3-Propyloxiranemethanol Acetate (5c). The epoxy alcohol (2.03 g, 17.5 mmol) was converted to the acetate in the usual manner. After flash chromatography a clear colorless liquid was obtained (2.54 g, 16.1 mmol, 92.0%): ^1H NMR δ 0.89–0.94 (t, 3, *J* = 7.0), 1.39–1.55 (m, 4), 2.05 (s, 3), 2.79–2.83 (m, 1), 2.90–2.94 (m, 1), 3.85–3.91 (dd, 1, *J* = 5.9, 6.3), 4.29–4.34 (dd, 1, *J* = 3.2, 9.0); ^{13}C NMR δ 13.7, 19.1, 20.6, 33.4, 55.1, 56.3, 64.7, 170.6.

Treatment of 5c with Telluride Ion. The epoxy acetate **5c** (1.32 g, 8.35 mmol) was treated with telluride ion obtained from Te (1.28 g, 10.0 mmol) and $LiEt_3BH$ (20 mL of 1.0 M solution, 20.0 mmol) at 0 °C. After 12 min, the reaction was complete, and only one product was observed on TLC and by ^1H NMR. (*E*)-2-Hexen-1-ol, **6c**, was obtained as a pale yellow oil after flash chromatography (0.68 g, 5.86 mmol, 70%): ^1H NMR δ 0.88–0.93 (t, 3, *J* = 7.4), 1.37–1.4 (m, 2), 2.01–2.03 (m, 2), 4.08–4.10 (d, 2, *J* = 4.8), 5.65–5.68 (m, 2); ^{13}C NMR δ 13.6, 22.3, 34.3, 63.8, 129.0, 133.3. The spectral data were identical with those reported previously.[31]

Reaction of (αS,2S)-α-*n*-Butyl-2-methyloxiranemethanol Acetate (5d) with Telluride Ion To Give (3*S*)-(−)-2-Methyl-1-hepten-3-ol [(3*S*)-(−)-6d]. (αS,2S)-α-*n*-Butyl-2-methyloxiranemethanol was obtained by SKR as previously described.[6,21] Epoxidation [(+)-DIPT] of racemic 2-methyl-1-hepten-3-ol (3.84 g, 30.0 mmol) for 6.5 h at −20 °C yielded the optically active glycidol,[28b,32] (αS,2S)-α-*n*-butyl-2-methyloxiranemethanol (1.83 g, 12.7 mmol, 42%): bp 35.8–36.4 °C (0.85 mm); $[\alpha]^{23}_D$ −11.8° (*c* 2.1, EtOH), $[\alpha]^{23}_D$ −3.4° (*c* 2.06, $CHCl_3$), 98% ee via ^1H NMR of MTPA ester: ^1H NMR δ 0.9–1.0 (t, 3, *J* = 7.2), 1.36–1.65 (m, 9), 2.6 (d, 1, *J* = 4.8), 2.9 (d, 1, *J* = 4.8), 3.68 (t, 1, *J* = 5.3); ^{13}C NMR δ 13.97, 18.09, 22.72, 27.72, 32.56, 50.26, 71.54. Racemic α-*n*-butyl-2-methyloxiranemethanol was prepared by epoxidation of the racemic allylic alcohol with TBHP–$VO(acac)_2$ and converted to MTPA ester (for comparisons with that of optically

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active glycidol): ^{1}H NMR of (*R*)-MTPA ester of the (±)-glycidol δ 2.11–2.13 (q, 1, *J* = 1.3, 9.1), 2.60–2.63 (q, 1, *J* = 1.3, 9.1), 3.42–3.43 (t, 3, *J* = 1.2), 3.46–3.47 (t, 3, *J* = 1.2), 4.80–4.85 (q, 1, *J* = 3.5, 4.8), 4.93–4.98 (q, 1, *J* = 4.1, 4.4). The remaining absorptions were identical with those of the optically active glycidol. The (–)-glycidol (1.6 g, 11 mmol) was converted to the acetate that was purified by distillation (Kugelrohr, 31–35.4°, 0.83 mm) (1.7 g, 9.2 mmol, 84%): $[\alpha]^{23}_D$ –14.3° (*c* 2.26, EtOH), $[\alpha]^{23}_D$ –17.4° (*c*, 1.60, $CHCl_3$), 98% ee via ^{1}H NMR with chiral shift reagent, Eu(hfc)$_3$,[33] including a comparison with racemic acetate: ^{1}H NMR δ 0.88–0.92 (t, 3, *J* = 6.6), 1.31 (s, 3), 2.56–2.58 (d, 1, *J* = 5.0), 2.78–2.80 (d, 1, *J* = 5.0), 4.58–4.62 (m, 1); ^{13}C NMR δ 13.89, 16.75, 20.97, 22.44, 27.52, 30.06, 53.06, 56.38, 75.58, 170.34.

Treatment of (–)-**5d** (0.39 g, 2.1 mmol) with telluride ion obtained from Te (0.27 g, 2.1 mmol) and $LiEt_3BH$ (4.2 mL of 1.0 M THF solution, 4.2 mmol) at 0 °C gave a pale yellow oil that was purified by flash chromatography (silica gel, 12:1 hexane/ether) to give (3*S*)-2-methyl-1-hepten-3-ol, (–)-**6d**, (0.25 g, 2.0 mmol, 94%): $[\alpha]^{24}_D$ –3.68° (*c* 3.6, EtOH) [lit.[21] $[\alpha]^{25}_D$ +3.84° (*c* 2.24, EtOH, for (*R*)-isomer). NMR spectra were identical with those of the racemate and of the (*R*)-enantiomer.

Reaction of *trans*-(±)-*erythro*- and *threo*-α-Cyclohexyl-3-methyloxiranemethanol Acetate (5e) with Telluride Ion To Give (*E*)-1-Cyclohexyl-2-buten-1-ol (6e). A 1.1:1 mixture of racemic *erythro*- and *threo*-α-2-cyclohexyl-3-methyloxiranemethanol[6,26] (1.08 g, 6.35 mmol) was converted to the acetate according to the general procedure. The diastereomeric acetates were separated by flash chromatography (silica gel, 1:10 ether/hexane). Erythro isomer (0.64 g, 3.0 mmol, 47%); ^{1}H NMR δ 1.00–1.33 (br m, 5), 1.27 (d, 3, *J* = 5.1), 1.60–1.80 (br m, 6), 2.04 (s, 3), 2.70 (4-line AB, 1, *J* = 2.1), 2.97 (8-line AB, 1, *J* = 2.1, 3.0), 4.53 (t, 1, *J* = 5.7); ^{13}C NMR δ 17.14, 20.85, 25.87, 25.93, 26.20, 27.76, 28.83, 40.30, 52.55, 57.84, 76.06, 170.21; IR (neat) 1740 (s), 1236 (s) cm^{-1}. Threo isomer (0.705 g, 3.33 mmol, 52%): ^{1}H NMR δ 0.09–1.30 (br m, 5), 1.29 (d, 3, *J* = 5.1), 1.60–1.80 (br, m, 6), 2.06 (s, 3), 2.76 (4-line AB, 1, *J* = 1.5), 2.97 (br 4-line AB, 1, *J* = 5.4), 4.47 (t, 1, *J* = 6.9); ^{13}C NMR δ 17.12, 20.90, 25.69, 25.77, 26.18, 28.55, 28.84, 39.94, 53.14, 59.12, 77.52, 170.38; IR (neat) 1740 (s), 1234 (s) cm^{-1}.

Treatment of an approximately 1:1 mixture of the *erythro*- and *threo*-acetates **5e** (0.100 g, 0.472 mmol) with telluride ion obtained by the reduction of Te with $LiEt_3BH$ according to the general procedure gave (*E*)-1-cyclohexyl-2-buten-1-ol, (*E*)-**6e** (51%, by NMR), and a small amount (9%) of (*E*)-4-cyclohexyl-3-buten-2-ol.[26] NMR also indicated the presence of unreacted erythro **5e**, the threo isomer being absent. No (*Z*)-1-cyclohexyl-2-buten-1-ol[26] was observed. The pure erythro isomer of **5e** (0.100 g, 0.472 mmol) was likewise treated with telluride ion for 6 h at room temperature to give (*E*)-**6e** (0.041 g, 0.241 mmol, 51%). *threo*-**5e** (0.100 g, 0.472 mmol) also gave (*E*)-**6e** (0.052 g, 0.377 mmol, 71%) after treatment with telluride ion for 1 h at room temperature.

Reaction of 2,3-Epoxygeranyl Acetate, 7a, with Telluride Ion. The acetate of racemic *trans*-3-methyl-3-(4-methyl-3-pentenyl)oxiranemethanol [(±)-2,3-epoxygeraniol] was prepared as described previously.[21] Reaction of the epoxy acetate, **7a** (3.30 g, 15.5 mmol), with telluride ion [Te (2.90 g, 23.3 mmol), $LiEt_3BH$ (48 mL, 1.0 M THF solution, 48 mmol)] was complete in 15 min at room temperature. Purification by flash chromatography (10:1 hexanes/ether) gave (±)-linalool (3,7-dimethyl-1,6-octadien-3-ol), **9a** (1.49 g, 9.67 mmol, 62%). The ^{1}H and ^{13}C spectra were identical with those reported previously.[3a,34] Geraniol (0.13 g, 0.86 mmol, 5.5%), **8a**, was a minor product identified by comparison of its spectroscopic properties with those of an authentic sample. A reaction of **7a** (2.12 g, 10.0 mmol) with telluride ion at 0 °C for 5 h gave the same products, linalool (0.71 g, 4.6 mmol, 46%) and geraniol (0.073 g, 0.47 mmol, 5%). The reaction of **7a** (2.12 g, 10.0 mmol) with telluride ion, produced by the reduction of Te with rongalite,[3a] gave after 50 h at room temperature linalool, **9a**, (0.52 g, 3.4 mmol, 34%), and 2,3-epoxygeraniol (0.22 g, 1.30 mmol, 13%).

The effect of fluoride ion on reactions performed with Te–$LiEt_3BH$ was investigated. Tetra-*n*-butylammonium fluoride (15 mL of 2.0 M solution in THF) was added to a suspension of lithium telluride prepared by reduction of Te (1.91 g, 15.0 mmol) with $LiEt_3BH$ (30 mL of 1.0 M solution in THF, 30.0 mmol) at 5 °C. The color of the reduction mixture changed from a chalky pink to a deep purple suggesting the possibility that some species[15] of telluride ion is being displaced from boron by fluoride ion. After 15 min, 2,3-epoxygeranyl acetate, **7a** (2.12 g, 10.0 mmol), in THF (10 mL) was added. No reaction occurred after 12 h at room temperature (TLC). After 30 h, 80% of the unreacted epoxygeranyl acetate was recovered along with a trace (5%) of linalool. No geraniol was detected.

Reaction of (±)-3,3-Dimethyl-α-*n*-hexyloxiranemethanol Acetate (7b) with Telluride Ion. 2-Methyl-2-decen-4-ol[35] (3.07 g, 18.1 mmol) was epoxidized (2 h) with TBHP (6.6 mL of 4.1 M stock solution in CH_2Cl_2, 27.1 mmol)–$VO(acac)_2$ (0.48 g, 1.81 mmol). An approximately equimolar mixture of *erythro*- and *threo*-epoxide was obtained after flash chromatography (silica gel, 5:1 hexanes/ether) as a colorless oil (3.23 g, 17.4 mmol, 96%): ^{1}H NMR δ 0.85–0.89 (t, 3, *J* = 4.3), 1.28–1.40 (br m, 14), 1.42–1.68 (m, 2), 2.51–2.55 (br s, 1, exchanges with D_2O), 2.64–2.66 (d, 1, *J* = 7.8), 2.68–2.71 (d, 1, *J* = 8.1), 3.42–3.49 (m, 1); ^{13}C NMR δ 14.0, 19.4, 22.6, 24.9, 25.0, 29.3, 31.7, 33.9, 59.7, 67.9, 70.4; IR (thin film) 3406, 1114, 1063 cm^{-1}.

The glycidol product (2.96 g, 15.9 mmol) was converted to a mixture of *threo*- and *erythro*-acetates (**7b**) (3.20 g, 13.1 mmol, 82%) in the usual way. Flash chromatography (40:1 hexanes/ether) partially separated the threo and erythro isomers,[36] the threo isomer being eluted first. Threo: ^{1}H NMR δ 0.83–0.87 (t, 3, *J* = 4.6), 1.19–1.39 (m, 14), 1.65–1.73 (m, 2), 2.05 (s, 3), 2.68–2.71 (d, 1, *J* = 8.2), 4.55–4.62 (m, 1); ^{13}C NMR δ 14.0, 19.1, 21.0, 22.5, 24.4, 24.6, 29.1, 31.6, 32.5, 59.1, 64.3, 71.9, 170.0; IR (thin film): 1736, 1238, 1023, 910 cm^{-1}. Erythro: ^{1}H NMR δ 0.85–0.89 (t, 3, *J* = 4.6), 1.27–1.50 (m, 14), 1.51–1.58 (m, 1), 1.63–1.69 (m, 1), 2.07 (s, 3), 2.77–2.80 (d, 1, *J* = 8.8), 4.71–4.79 (m, 1); ^{13}C NMR: δ 14.0, 19.5, 21.1, 22.5, 24.6, 24.7, 29.1, 31.6, 32.0, 58.8, 64.7, 73.3, 170.4.

An approximately 1:1 mixture of *erythro*- and *threo*-acetates (**7b**) (0.92 g, 3.77 mmol) was treated with telluride ion from Te and $LiEt_3BH$ according to the general procedure. After 24 h, only 66% reaction had occurred. Flash chromatography (hexanes/ether (15:1)) gave three fractions. The first was unreacted starting material (**7b**) (0.32 g, 1.3 mmol, 34%), the second was transposed product, *trans*-2-methyl-3-decen-2-ol[35] (*trans*-**9b**) (0.12 g, 0.70 mmol, 18%), and the third was a mixture (0.31 g, 1.8 mmol, 48%) of *cis*-2-methyl-3-decen-2-ol (*cis*-**9b**) and the deoxygenated product, 2-methyl-2-decen-4-ol (**8b**). TLC showed one spot, but ^{1}H NMR indicated a 1:1 ratio of **8b** to **9b**. *trans*-2-Methyl-3-decen-2-ol (*trans*-**9b**): ^{1}H NMR δ 0.85–0.90 (t, 3), 1.22–1.35 (m, 8), 1.37 (s, 6), 1.47–1.50 (br s, 1), 2.29–2.31 (m, 2), 5.28–5.35 (m, 1), 5.45–5.49 (dt, 1, *J* = 1.4, 11); ^{13}C NMR δ 14.1, 22.6, 28.1, 29.1, 30.1, 31.1, 31.8, 71.6, 131.4, 136.7. *cis*-2-Methyl-3-decen-2-ol (*cis*-**9b**): ^{1}H NMR δ 0.84–0.88 (t, 3), 1.14–1.43 (m, 14), 1.51–1.61 (br s, 1), 1.98–2.04 (m, 2), 5.60–5.62 (AB d, 2); ^{13}C NMR δ 14.1, 22.6, 28.8, 29.8, 31.6, 31.7, 32.1, 70.6, 127.3, 137.8. 2-Methyl-2-decen-4-ol (**8b**): ^{1}H NMR δ 0.84–0.88 (t, 3), 1.14–1.43 (m, 14), 1.51–1.61 (br s, 1), 1.28 (s, 3), 1.30 (s, 3), 4.32–4.35 (m, 1), 5.14–5.18 (dt, 1).

Reaction of (–)-3,3-Dimethyl-α-*n*-hexyloxiranemethanol Acetate [(–)-7b] with Telluride Ion. 2-Methyl-2-decen-4-ol[35] (1.70 g, 10.0 mmol) was subjected to SKR [1.5 h, (+)-DIPT (0.28 g, 1.2 mmol), $Ti(OiPr)_4$ (0.28 g, 1.0 mmol), TBHP (0.9 mL of 5.5 M solution in isooctane, 5.0 mmol), 4A molecular sieves (0.51 g)] followed by the simplified aqueous workup procedure.[21] Purification of the crude product (2.6 g) by flash chromatography (silica gel, hexanes/ethyl acetate (10:1)] yielded the resolved allylic alcohol (0.75 g, 4.42 mmol, 44%), and the desired glycidol (1*S*, 2*S*)-3,3-dimethyl-α-*n*-hexyloxiranemethanol (0.84 g, 4.5 mmol, 45%, >95% ee via ^{1}H NMR of MTPA ester): $[\alpha]^{21}_D$ –3.20° (*c* 1.47, $CHCl_3$); ^{1}H NMR δ 0.85–0.89 (t, 3, *J* = 4.3), 1.28–1.40 (br

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m, 14), 1.42–1.68 (m, 2), 2.51–2.55 (br s, 1, exchanges with D_2O), 2.68–2.71 (d, 1, J = 8.1), 3.42–3.49 (m, 1).

The glycidol (0.81 g, 4.4 mmol) was converted to the *erythro*-acetate (–)-**7b** (1.03 g, 4.2 mmol, 96%): $[\alpha]^{21}_D$ –1.89° (*c* 2.43, $CHCl_3$); ^1H NMR δ 0.85–0.89 (t, 3, J = 4.6), 1.27–1.50 (m, 14), 1.51–1.58 (m, 1), 1.63–1.69 (m, 1), 2.07 (s, 3), 2.77–2.80 (d, 1, J = 8.8), 4.71–4.79 (m, 1). Treatment of (–)-**7b** (0.89 g, 3.6 mmol) with telluride ion obtained from Te (0.55 g, 4.3 mmol) and $LiEt_3BH$ (8.6 mL of 1.0 M solution in THF, 8.6 mmol) for 24 h resulted in 67% reaction. Flash chromatography (20:1 hexanes/ether) gave a 1:1 mixture of (0.45 g, 2.6 mmol, 72%) **8b** and **9b**. [(*Z*)-2-Methyl-3-decen-2-ol, **9b**]: ^1H NMR δ 0.84–0.88 (t, 3), 1.14–1.43 (m, 14), 1.51–1.61 (br s, 1), 1.98–2.04 (m, 2), 5.60–5.62 (AB d, 2); ^{13}C NMR δ 14.1, 22.6, 28.8, 29.8, 31.6, 31.7, 32.1, 70.6, 127.3, 137.8. [(2*S*)-2-Methyl-2-decen-4-ol, **8b**]: ^1H NMR δ 0.84–0.88 (t, 3), 1.14–1.43 (m, 14), 1.51–1.61 (br s, 1), 1.28 (s, 3), 1.30 (s, 3), 4.32–4.35 (m, 1), 5.14–5.18 (dt, 1, J = 1.3, 8.8); ^{13}C NMR δ 14.0, 18.2, 22.6, 25.4, 25.7, 29.3, 31.8, 37.7, 68.7, 128.3, 134.9.

Acknowledgment. We thank the National Science Foundation (CHE-9102998), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Syracuse University for support for this research. We are indebted to Professor John Baldwin for the use of a polarimeter.