6c at 60 °C is 850 times faster in acetonitrile than in cyclohexane,[5] suggesting the gauche zwitterion **4** as an intermediate. The half-life of **14** at 40 °C amounted to 138 h in CS_2 and 35 h in $CDCl_3$. Products were the *trans*-thiolane **17** and the *trans*-cyclopropane **18** in the time-independent ratio of 78:22 (kinetic control); in addition, the ^1H NMR spectrum showed the methyl singlet of thione **9**. An equilibration of the gauche zwitterion **15** with anti conformation **16** is assumed. The cyclopropane formation is interpreted by an intramolecular nucleophilic substitution of **16**, thione **9** being the leaving group. The preference for the trans structures of **17** and **18** may result from steric factors.

In contrast to **4c** → **6c**, the ring closure **15** → **17** is reversible. In benzonitrile at 80 °C, **17** is converted to **18** + **9** with a half-life of 13 h. The thermodynamic preference of **18** + **9** must be due to the loss of steric strain in the indane-spiro-thiolane **17** and the entropy factor (two molecules from one), thus outweighing the ring strain of cyclopropane **18**.

The isolation of **17**, mp 113 °C, required removal of **18** + **9** by distillation. The CF_3 groups of **17** appear at δ_F -58.2 and -63.9 ($J_{F,F}$ = 11.6 Hz), less different than in **14** (-55.6, -73.7). After thermolysis of **17** (140 °C, neat), cyclopropane **18**, mp 58-59 °C, was sublimed at 40-50 °C. The singlet of 3-H_2 at δ 2.46 is broadened by H,F coupling. The CF_3 groups form a singlet at δ -66.2 in the ^1H-decoupled ^{19}F NMR spectrum.

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Stereospecific Telluride-Mediated Conversion of Glycidols to Allyl Alcohols: An Extension of the Sharpless Kinetic Resolution

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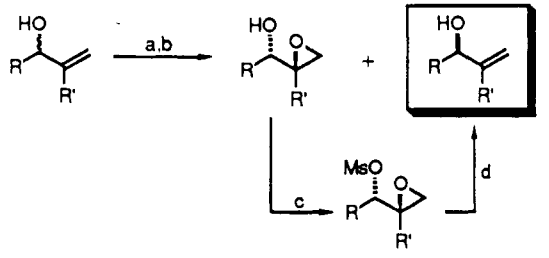
Summary: Treatment of methanesulfonate esters of terminal glycidols obtained by epoxidation in the Sharpless kinetic resolution (SKR) of 1-substituted 2-propenols (secondary allyl alcohols) with telluride ion (Te^{2-}) converts the glycidols to allyl alcohols of the same stereochemical configuration as the unreacted enantiomer from the SKR.

The Sharpless kinetic resolution (SKR) of secondary allyl alcohols,[1] like all resolutions, is limited to a theoretical yield of 50% of one enantiomer from the racemic mixture. In the Sharpless procedure, one enantiomer of the allyl alcohol is converted to a glycidol, leaving the slower reacting enantiomer virtually untouched. The mixture is easily separated, and the allyl alcohol and the glycidol of high optical purity can be obtained when the relative rates of epoxidation of the two enantiomers are sufficiently different. We report that the glycidol, whose carbinol carbon atom has a configuration opposite to that of the allyl alcohol, can be converted to the same allyl alcohol obtained in the kinetic resolution. The process involves an application of telluride chemistry used in our earlier, general synthesis of allyl alcohols.[2] This combination of the SKR and our telluride method effects a conversion of a racemic allyl alcohol to a single enantiomer, the theoretical yield being 100%. The inversion of configuration that occurs in the telluride-mediated reactions that we have studied is complete, and the yields of allyl alcohol in this process are generally high (typically 87-93%, although in one case a 69% yield was obtained). Combined yields of allyl alcohol from both the kinetic resolution and telluride steps range from 75-88%.[3]

The glycidol product in the SKR is converted to the methanesulfonate ester by the action of methanesulfonic anhydride and pyridine, followed by treatment with telluride ion generated by the in situ reduction of the element by sodium hydroxymethanesulfinate dihydrate (Rongalite).[4] The overall transformation that occurs is the deoxygenation of the epoxide with concurrent inversion of the carbinol center to give the desired allyl alcohol. Deoxygenations by tellurium reagents of epoxides that do not bear proximate leaving groups have been reported previously.[5,6]



(1)[7]

(a) Ti(O-*i*-Pr)$_4$, TBHP, (+)- or (-)-DIPT, CH_2Cl_2; (b) chromatographic separation (silica gel); (c) $(CH_3SO_2)_2O$, pyridine, DMAP, CH_2Cl_2; (d) Te (1.1 equiv), $HOCH_2SO_2Na{\cdot}2H_2O$ (3 equiv based on tellurium), NaOH (5 equiv based on tellurium, 1 N), 50 °C, 2 h; cool to room temperature; add mesylate in THF.

Although there are a number of methods for inverting carbinol carbon centers, we know of no single-step procedure to deoxygenate an epoxide and invert an adjacent carbinol center. Furthermore, the tellurium from these reactions is recovered and may be reused. If the epoxy alcohol is desired, the allyl alcohol from the SKR may be epoxidized, inverted via the telluride method, and re-epoxidized under the conditions for the Sharpless asymmetric epoxidation.[1a]

(1) (a) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765-5780. (b) Rossiter, B. E. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, pp 193-243. (c) Finn, M. G.; Sharpless, K. B. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985, Vol. 5, pp 247-301.

(2) Polson, G.; Dittmer, D. C. *Tetrahedron Lett.* **1986**, *27*, 5579-5582.

(3) The deviation from 100% ee is the result of the kinetic resolution step and depends on the relative rates of epoxidation of the two enantiomers of the allyl alcohol. The overall yields suffer both in the epoxidation step and in the telluride step. However, no attempts were made to optimize them.

(4) Tschugaef, L.; Chlopin, W. *Ber.* **1914**, *47*, 1269-1275.

(5) Clive, D. L. J.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2347-2354.

(6) Barton, D. H. R.; Fekih, A.; Lusinchi, X. *Tetrahedron Lett.* **1985**, *26*, 6197-6200.

(7) When R = Ph (eq 1), the telluride reaction fails, possibly because of an intervening S_N1 reaction.

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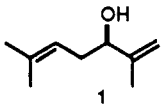
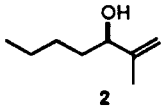
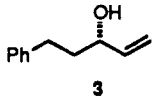
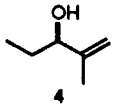
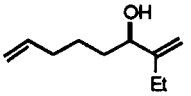
Table I. Allyl Alcohols from the SKR-Telluride Procedure

allyl alcohol	% ee[a]	$[\alpha]_D^{24}$	% yield[b]
 1	92	+25.4°	79
 2	94	+3.61°	88
 3	92	+4.96°	75
 4	≥98	+4.80°	78
 5	95	+10.2°	82

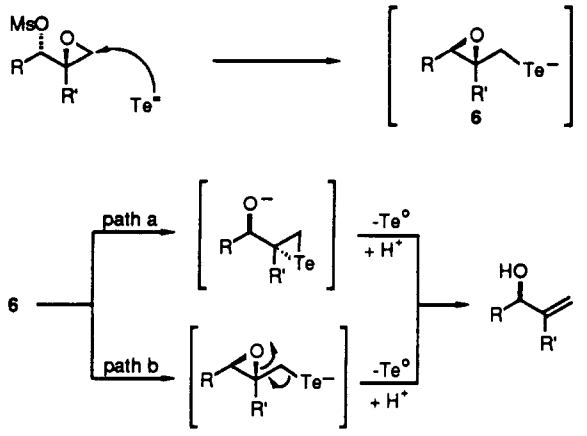
[a] % ee based on ^{1}H NMR analysis of the (+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid ester. [b] Isolated yield of the total amount of enantiomerically pure allyl alcohol is based on the weight of the starting racemate.

Table I lists examples of optically active allyl alcohols that have been obtained by the SKR-telluride process. The acetate of allyl alcohol, 1, is the sex pheromone of the Comstock mealybug, *Pseudococcus comstocki*.[8] Alcohol 3 is a precursor to the enantiomerically pure starting material for the synthesis of the pheromone of *Trogoderma granarium*,[9] and 4 is the opposite enantiomer of the starting material for the synthesis of (+)-pumilitoxin-A, which was accomplished recently by Overman and Lin.[10]

This method affords not only a useful synthetic strategy but also a stereochemical mechanistic probe for the telluride-mediated conversion of glycidol derivatives to allyl alcohols. Scheme I illustrates two possible mechanisms for this conversion. Epitellurides have been suggested as unstable intermediates in the formation of alkenes from epoxides via tellurium compounds.[5,6]

Coupling of telluride chemistry with the Sharpless kinetic resolution of secondary allyl alcohols provides a powerful method for the conversion of a racemic allyl alcohol to either enantiomer in high yield and high enantiomeric purity. Within the limits of experimental manipulations, none of the original racemic allyl alcohol is wasted. The percent enantiomeric excess that is obtained is limited only by the relative rates of epoxidation in the kinetic resolution step. Our synthesis of single enantiomers in high yield and high enantiomeric excess may enable more efficient syntheses of many natural products that previously had to contend with a 50% yield step in the separation of two enantiomers.[11]

Scheme I



It previously has been reported by us[12] and by others[13] that epichlorohydrins (chloromethyloxiranes) are converted to allyl alcohols via sodium iodide in acetone, analogously to the conversion with sodium telluride. Attempts at reaction of sodium iodide with secondary glycidyl mesylates have been unsuccessful in our hands. At this time, the telluride technique is limited to secondary allyl alcohols in which the oxirane ring is terminal, but our recent work suggests that glycidyl mesylates and tosylates derived from allyl alcohols of other substitution patterns react with telluride ion but give products that are different from those presented here. These results will be reported at a later date.

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Supplementary Material Available: A full Experimental Section plus ^{1}H NMR, ^{13}C NMR, and IR spectral data for compounds 1–5 and for the corresponding glycidols (7 pages). Ordering information is given on any current masthead page.

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(9) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Taketani, M.; Viti, S. M.; Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589–604.
(10) Overman, L. E.; Lin, N.-H. *J. Org. Chem.* **1985**, *50*, 3669–3670.
(11) (a) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 6682–6690. (b) Evans, D. A.; Bender, S. L.; Morris, J. *J. Am. Chem. Soc.* **1988**, *110*, 2506–2526.
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(13) Barluenga, J.; Fernandez-Simon, J. L.; Concellon, J. M.; Yus, M. J. *J. Chem. Soc., Perkin Trans. 1* 1989, 77–80.