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Tellurium in the "No-Solvent" Organic Synthesis of Allylic Alcohols

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Abstract: Elemental tellurium can be reduced by rongalite (HOCH₂SO₂Na•2H₂O)-KOH in the solid phase by application of ultrasound or by microwave irradiation. Without solvent, the organic substrate (eg sulfonate ester of an oxiranemethanol) is added with further sonication or irradiation to yield the desired organic product (eg allylic alcohols) and elemental Te which may be recycled. Phase-transfer conditions (water-toluene) also are satisfactory. © 1997 Elsevier Science Ltd.

INTRODUCTION

Elemental tellurium is relatively non-toxic¹ and inexpensive [roughly \$45 per mole (128 g) as 200 mesh powder]². Two properties in particular commend its use in synthesis: (1) telluride ion, formed by the reduction of the element,³ is a powerful nucleophile that is attracted to electrophilic sites in organic substrates⁴ and (2) the element is relatively more thermodynamically stable than Te^{2-5} so that if a reasonable, not too energetic pathway for formation of Te^o is available in an organic telluride intermediate it is likely to be taken.

An overall process given in Scheme 1 may be termed a "nucleophilic reduction", a term first suggested to us by Dr. Douglas A. Livingstone. Tellurium may be used in either stoichiometric or catalytic quantities, the latter of course requiring a stoichiometric amount of reducing agent. The reduced tellurium may consist of a mixture of purple anions $Te_n^{2-.6}$ A number of other nucleophilic reductions induced by telluride have been reported.⁷⁻²⁴



Scheme 1. The Nucleophilic Reduction Process.

Alkenes

Farrar and Gulland described the dehalogenation of *vic*-dibromides with Te^{2-} , an early example of a nucleophilic reduction with telluride ions (Eq 1).⁷ The reaction may be viewed either as a nucleophilic attack on a carbon or bromine atom or as single electron transfer reaction from Te^{2-} to an antibonding molecular orbital of the dihalide.

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Clive and Wickens reported a reaction with *vic*-disulfonates, analogous to that shown in Eq. 1 for a *vic*dibromide which they applied to the preparation of 2,' 3'-didehydro-2', 3'-dideoxynucleosides (Eq 2).²² Recently, we reported the conversions of cyclic sulfates of *vic*-diols to alkenes under relatively mild conditions (0 °C or rt, 5 min to 2.5 h) and with high stereoselectivity (Eq 3).²⁵ Cyclic sulfates are readily obtained by the procedure of Sharpless and Gao (SOCl₂, NaIO₄, RuCl₃•3H₂O).²⁶ Cyclic thionocarbonates and carbonates also yielded alkenes on treatment with telluride ion but the procedure seemed less general. Previously, cyclic sulfates of *vic*-diols have been converted to alkenes by treatment with sodium naphthalenide in THF with low stereospecificity; the method failed with the cyclic sulfate of diethyl (*L*)-(-)-tartrate.²⁷ Alkenes also have been obtained from cyclic sulfates via a selenocyanate instead of telluride.²⁸ These telluride reactions and other reactions to be described may proceed via an epitelluride, expected to be a thermally unstable species by analogy with episelenides.²⁹ The only known stable epitellurides involve ring atoms other than carbon.³⁰ Epitellurides have been proposed as intermediates in a number of reactions.^{14, 21, 31}



Allylic Alcohols

The Katsuki-Sharpless asymmetric epoxidation of allylic alcohols mediated by a titanium-tartrate complex is a powerful and convenient procedure for introducing chirality into organic molecules.³² Several limitations of the Sharpless procedure can be overcome by application of the tellurium nucleophilic reduction process of Scheme 1^{33, 34} that was first applied to the synthesis of 2-substituted allylic alcohols from epichlorohydrins.³³ These limitations and how they were avoided are exemplified in Schemes 2-6.³⁴ As shown in Schemes 3 and 5, in addition to avoidance of the 50% yield limitation in a Sharpless kinetic resolution one also avoids the slow

epoxidation that occurs with a monosubstituted double bond when attempting to resolve racemic 1 or 3. A putative mechanism that is applicable to other schemes is included in Scheme 3.



Scheme 2. Avoidance of the 50% Limitation in the Kinetic Resolution of a Secondary Allylic Alcohol (Method 1).



Scheme 3. Avoidance of the 50% Limitation (Method 2).



Scheme 4. Avoidance of the Failure of Tertiary Allylic Alcohols (eg Racemic 2) in a Katsuki- Sharpless Kinetic Resolution.



Scheme 5. Avoidance of Difficulty in the Kinetic Resolution of Allylic Alcohols with Bulky Tertiary Alkyl Groups on the Carbinol Carbon Atom (eg Racemic 3).



Scheme 6. Avoidance of Potential Low Enantioselectivity in the Kinetic Resolution of Cis, Secondary Allylic Alcohols (eg Racemic 4).

These tellurium processes have been applied to the synthesis of (3R)-(-)-linalool^{34a} (this enantiomer of 2 was previously obtained in nine steps from a resolved precursor³⁵), (R)-(+)-2,6-dimethyl-1,5-heptadiene-3-ol^{34a} (the acetate of which is a pheromone of the Comstock mealybug), the lactone functionality (with two chiral centers) of mevinic acids related to cholesterol-lowering drugs,³⁶ and the optically active sugar, boivinose,³⁷ previously synthesized in racemic form.³⁸

The tellurium procedure has been adapted for use with as little as 10 mol % of telluride ion in conjunction with excess reducing agent.³⁹ In this way (S)-(+)-linalool is obtained in 97% yield from (2S, 3S)-epoxygeraniol tosylate in aqueous THF.

Allylic Amines

N-Substituted aziridinemethanols, nitrogen analogs of the oxiranemethanols discussed in the previous section, can be converted to allylic amines by conversion to the O-tosylate or mesylate and subsequent treatment with telluride ion.⁴⁰ Among other uses, allylic amines are important intermediates in the synthesis of α - or β -amino acids.⁴¹ Best results occur when the substituent on nitrogen is not an electron-withdrawing group (eg Ts) since such molecules present an attractive opportunity for telluride ion to attack one of the ring carbon atoms instead of, or in addition to, the carbinol carbon atom of the O-tosylate. An N-trityl or N-benzhydryl group gives satisfactory results. Equations 4-6 show examples of the telluride procedure with Eq 4 illustrating a possible mechanism. When tellurium is reduced with rongalite (HOCH₂SO₂Na•2H₂O) results are not very satisfactory, but the yields are improved by use of sodium borohydride in DMF for the reduction. This suggests that perhaps the borane-trimethylamine complex formed as a byproduct³⁶ is acting as a mild Lewis acid catalyst.



Aziridine 5 with an electron-withdrawing *t*-butoxycarbonyl (Boc) substituent on nitrogen yielded under phase-transfer conditions an isomerized product 6, analogous to the isomerization of a vinylglycine derivative reported by Rapoport and Afzali-Ardakani.⁴²



RESULTS AND DISCUSSION

Environmental concerns are becoming increasingly important in the development of new organic chemical processes. Our previous tellurium-mediated transformations described in the introduction have aspects that are desirable from an environmental standpoint: (1) the tellurium is recyclable and it can be used in catalytic amounts; (2) the reducing agent rongalite is presumably converted to a water-soluble, non-toxic bisulfite derivative; (3) a largely aqueous organic medium can be employed when rongalite is the reducing agent with only small amounts of organic solvent, typically THF, needed to disperse the water-insoluble organic substrate. To perform reactions in the absence of organic solvents is even more environmentally desirable because the disposal or recovery of these solvents is reduced or eliminated⁴³. The use of an aqueous medium as much as possible is also environmentally beneficial.

"No-solvent" Reactions via Ultrasound and Microwave Techniques.

We discovered recently that elemental tellurium can be reduced in the absence of solvent by trituration of Te, HOCH₂SO₂Na•2H₂O, and KOH in a mortar in an inert atmosphere (Ar or N₂).⁴⁴ This initial process has been improved (1) by the addition of alumina, 4A molecular sieves, TiO₂, or hydroxyapatite [Ca₅(PO₄)₃OH] which minimizes the sticky nature of the original telluride mixture caused in part by the KOH and (2) by the use of a simple ultrasonic cleaning bath⁴⁵ to allow the solid mixture to react at ambient temperature. After 1.5 to 2 h, the mixture had the red-purple color of telluride ions. Once the tellurium has been reduced in the solid phase, neat substrate (solid or liquid) is mixed with the telluride reagent and sonicated further until the reaction is complete as indicated by thin layer chromatography or ¹H NMR spectroscopy. The most rapid reactions occurred when the telluride-oxiranemethanol tosylate combination was irradiated with microwaves. Table 1 lists some substrates (racemic) that have been investigated. They all have previously undergone the telluride nucleophilic reduction transposition to allylic alcohols in solution.³⁴ Racemic starting materials were used for convenience in optimizing the methods, but no difficulty is foreseen if optically active substrates are employed as in the previous solution work.

$$R^{3} \xrightarrow{O}_{R^{1}} O_{Ts} \xrightarrow{Te^{2}(Te^{0}, HOCH_{2}SO_{2}Na \cdot 2H_{2}O, KOH)}_{ultrasound or microwaves} R^{3} \xrightarrow{OH}_{R^{2}} R^{1} + Te^{0}$$
⁽⁸⁾

Entry	R ¹	R ²	R ³	Conditions	t, min	Yield, % (isolated)
1	Н	<i>n</i> -C ₅ H ₁₁	н	Al ₂ O ₃ ª	150	> 95
2	н	<i>n</i> -C ₆ H ₁₃	н	Al ₂ O ₃ ª	720	90 ^b
3	СӉ	Ph	н	tartaric acid ^a	60	85
4	CH₃	Ph	н	c	14	50 ^{d,e}
5	н	کر ∕ےر	CH3	Al ₂ O ₃ ª	120	86 ^f
6	н	کر کر	CH3	c	9.5	83
7	н		CH3	Al ₂ O ₃ ª	360	89

Table 1. "No-Solvent" Reactions Involving Telluride Ion (Eq. 8).

a) Ultrasonic bath . b) One-pot reaction. c) Microwave, 525 W. d) Reaction was interrupted before completion.

e) Yield by ¹H NMR. f) In a one-pot reaction with catalytic Te, a 90% yield was obtained in 720 min.

Under conditions in Table 1 are listed the solids added with the KOH in the tellurium reduction step. In addition to helping the reaction to be more free-flowing (sometimes the mixture still may retain a "sticky" character particularly if liquid substrates are added), the solids may function catalytically as Lewis acids. Why the farnesyl derivative, Entry 7, took somewhat longer to react is unclear. One possibility is that the long hydrocarbon chain reduces the efficiency of mixing with the polar telluride mixture. Inactivated 4A molecular sieves also functioned well in place of alumina, and the reactions were a little faster. Titanium dioxide and hydroxyapatite can also replace alumina but no particular advantage in doing so has yet materialized. A very small rotation that was observed in the product when tartaric acid was used (Entry 3) was caused by traces of tartaric acid that was not completely removed during workup. The fastest reactions occurred when the reaction mixture was irradiated with microwaves⁴⁶.

A one-pot procedure shows promise. In this method all reagents (substrate, Te⁰, rongalite, and KOH) are mixed and ultrasonicated. The telluride reacts with the neat oxiranemethanol tosylate as the former is produced

by reduction of Te⁰. Since the elemental Te⁰ that is extruded during the reaction is more finely divided than the original 200 mesh Te⁰, it may be expected to be reduced more efficiently. However, the one-pot reactions investigated so far are slow (overnight).

Reactions Under Phase Transfer Conditions.

The transformation of an epoxytosylate to an allylic alcohol also can be performed conveniently and in high yield under phase transfer conditions in which an aqueous phase plays an important role. In this procedure, a suspension of Te^o is reduced in aqueous rongalite-NaOH at 60 °C under argon to give a deep redpurple solution. After this mixture is cooled to room temperature, the phase transfer catalyst, Adogen 464, and the oxiranemethanol tosylate in toluene are added. Black elemental tellurium was observed after 15 min of stirring. After about 2 h, stirring was stopped and the toluene layer containing the allylic alcohol product was separated. The allylic alcohol is obtained in pure form by removal of the toluene. A catalytic amount of Te^o can be used, and the aqueous layer containing suspended tellurium remaining after the reaction can be reused by addition of more rongalite and NaOH. Table 2 lists the racemic substrates that were investigated.

 Table 2. Allylic Alcohol Synthesis (Eq. 8) via Telluride Ion and Oxiranemethanol Tosylates Under Phase-transfer Conditions.

Entry	R ¹	R ²	R ³	Yield, % (isolated)
1	Н	Ph	н	97
2	CH3	Ph	Н	99ª
3	Н	<i>n</i> -C ₅ H ₁₁	н	93
4	Н	<i>n</i> -C ₆ H ₁₃	Н	98
5	Н	 کرد	CH3	90
6	н		CH₃	96

a) Yield with a catalytic amount (13 mole%) of Te instead of stoichiometric or excess was 94%. For best results the reaction was heated (65 °C) and stirred vigorously.

"No-solvent" Reactions via Mortar and Pestle.

Trituration of Te⁰, rongalite, and KOH in a mortar (glove bag, N₂ or Ar), transferal of the mixture to a flask, and heating of the sealed flask outside of the glove bag (80 $^{\circ}$ C) for 3 h gave a purple telluride mixture.

The sticky telluride reagent and oxiranemethanol tosylate were triturated together in a mortar (glove bag, N₂ or Ar) periodically for about an hour, black Te⁰ being observed within 5 min. Table 3 shows the results. In addition to the tosylates of primary oxiranemethanols, a secondary substrate, 7, also performed well (Eq. 9) as did a cyclic substrate (Entry 7). Epoxyditosylate 8 also reacted and the ¹H NMR spectrum of the product is consistent with the formation of butadiene monoxide (Eq. 10). An isolated yield has not yet been obtained because of the volatility of the product.



We now prefer the techniques involving ultrasound, microwave, or phase-transfer catalysis to the mortar and pestle method because the former are more reliable. One trituration experiment in the mortar is not always reproduced by the next, and the variable stickiness of the reaction mixture is a drawback.

Entry	R ¹	R ²	R ³	Yield, % (isolated)
1	Н	Ph	Н	60 ^{a,b}
2	CH3	Ph	Н	97
3	Н	<i>n</i> -C ₅ H ₁₁	н	83
4	н	<i>n</i> -C ₆ H ₁₃	H	95
5	н)= (CH3	76
6	Н	کے کے	CH3	96
7	—(СН	2)4 —	Н	87

Table 3. Allylic Alcohol Synthesis (Eq. 8) via Trituration of Neat Reagents in a Mortar.

a) Cinnamyl alcohol (22%) also was obtained. b) (2-R, 3-R)-3-phenyl-2-oxiranemethanol tosylate gave (S)-1-phenyl-2-propene-1-ol (45%).

CONCLUSIONS

The tellurium mediated nucleophilic reduction process (Scheme 1) under "no-solvent" (in an ultrasound bath or microwave oven) or phase-transfer conditions is convenient and rapid, especially for the "one-pot" procedure and under microwave irradiation in the solid phase. The "no-solvent" process is environmentally "friendly" because the use of an organic solvent is avoided in the telluride reaction (although solvent may be used in extraction of the product), the elemental tellurium is not consumed and can be used in less than stoichiometric amounts (but a longer reaction time is needed for catalytic amounts of Te⁰), and the phase-transfer conditions employ an aqueous phase (but also an organic phase). The procedures are applicable to a variety of substrates providing they have an electrophilic site (not too sterically hindered) to attract Te²⁻ and that a relatively low energy pathway exists for the extrusion of elemental tellurium.

EXPERIMENTAL SECTION

All reactions were performed under an inert atmosphere (N₂ or Ar). A glove bag was used for mixing reagents. Chemicals were obtained commercially and used as supplied. Free-flowing mixtures of KOH adsorbed on Al₂O₃ (Grade I), TiO₂, or Ca₅(PO₄)₃(OH) were prepared by dissolving KOH (10.0 g, 178 mmol) in methanol (30 mL). Addition of the solid adsorbant (20 g) was followed by evaporation of the methanol at 50-60°C by means of a rotary evaporator. Mixing of reagents prior to reaction was done in a glove bag under nitrogen in a mortar with either a spatula or a pestle. Oxiranemethanol tosylates and all products of the telluride reactions have been prepared previously and their physical properties are in agreement.³⁴ Epoxidations were performed with *m*-chloroperbenzoic acid³⁴ or *t*-butylhydroperoxide-vanadyl acetylacetonate.⁴⁷ Reactions were monitored by TLC (silica gel) with visualization by ultraviolet light and/or anisaldehyde stain.

Ultrasonication was done in a Branson 1400 ultrasound bath and microwaving was done in a Tappan Model 10 oven⁴⁸. ¹H NMR spectra were taken at 300 MHz in CDCl₃.

General Procedure for Reduction of Te^o Under Ultrasonication.

Tellurium (1.021 g, 7.990 mmol, or 1 equiv), KOH-Al₂O₃ (4.04 g; 24.00 mmol KOH, or 3 equiv) and rongalite (HOCH₂SO₂Na•2H₂O) (3.70 g, 24.0 mmol, or 3 equiv) were mixed. After 10-20 s the mixture was transferred to a round-bottomed or flat-bottomed flask, and the flask was sealed under N₂. Ultrasonication for 2-3 h resulted in a red-purple solid (Te_n^{-2}). The same procedure was used for TiO₂, Ca₅(PO₄)₃(OH), and 4A molecular sieves.

General Procedure for Reduction of Teo Under Microwave Irradiation.

Tellurium (0.51 g, 4.0 mmol), KOH-Al₂O₃ (2.02 g, 12.0 mmol KOH) and rongalite (1.849 g, 12.00 mmol) were mixed as described above and transferred to a beaker sealed under N₂ (plastic wrap). Irradiation at full power (*ca* 525 W) for 5-7 min resulted in a red-purple mixture containing Te_n^{2-} . The same procedure was used with Ca₅(PO₄)₃(OH).

Reaction of Oxiranemethanol Tosylates with Telluride Ion Under Ultrasonication.

The tosylate (1 equiv) was mixed with telluride ions (2 equiv) prepared as described above. After 30-40 s the reaction mixture was transferred to the flask in which the Te^o was reduced and was sealed under N₂. During sonication small samples were removed and analyzed by ¹H NMR or by TLC. When the reaction was complete, the contents of the flask were exposed to air to convert the remaining unreacted telluride ions to elemental Te. Water (a few drops) was added and the mixture was extracted with ether (5x10 mL). The ether extracts were filtered through Celite to remove traces of Te^o and insoluble inorganic substances and dried

(Na₂SO₄ or MgSO₄). Removal of the ether by evaporation gave the allylic alcohol in good purity whose spectroscopic properties were identical with those of known substances.³⁴

Linalool (3, 7-Dimethyl-1, 6-octadien-3-ol). The oxiranemethanol tosylate (0.445 g, 1.37 mmol) derived from geraniol (3, 7-dimethyl-2,6-octadien-1-ol) was sonicated for 2 h with the telluride mixture from the reduction of Te^o (0.52 g, 4.1 mmol) to give linalool (0.181 g, 1.17 mmol, 86%).

2-Methyl-1-phenyl-2-propen-1-ol. The oxiranemethanol tosylate (0.900 g, 2.83 mmol) derived from (E)-2-methyl-3-phenyl-2-propen-1-ol was sonicated for 1 h with the telluride mixture from the reduction of Te^o (1.02 g, 7.99 mmol) to give the product (0.354 g, 2.41 mmol, 85%).

1-Octene-3-ol. The oxiranemethanol tosylate (0.624 g, 2.21 mmol) derived from 2-octen-1-ol was sonicated for 2.5 h with the telluride mixture from the reduction of Te^o (1.02 g, 7.99 mmol) to give the crude product (0.30 g, 2.3 mmol, ~100%).

Nerolidol (3, 7, 11-Trimethyl-1, 6, 10-dodecatrien-3-ol). The oxiranemethanol tosylate (0.80 g, 2.0 mmol) derived from farnesol (3, 7, 11-trimethyl-2, 6, 10-dodecatrien-1-ol) was sonicated for 6 h with the telluride mixture from Te^o (0.51 g, 4.0 mmol) to give nerolidol (0.401 g, 1.81 mmol, 89%). Reaction of Oxiranemethenol Tosylates with Telluride Ions Under Microwave Irradiation.

The oxiranemethanol tosylate (2 mmol, or 1 equiv) was mixed with Te²⁻ (2 equiv) as described above. The reaction mixture was transferred to the beaker (50 mL) in which the Te⁰ was reduced, the contents of the beaker under N₂ were sealed with plastic wrap and microwaved. A sample was withdrawn every 3-4 min and analyzed by TLC or ¹H NMR. Workup was as described for the ultrasound reactions.

Linalool. Tellurium (0.510 g, 4.00 mol) was reduced under microwave irradiation by rongalite (1.849 g, 12.00 mmol) -KOH (0.673 g, 12.0 mmol)-Al₂O₃(1.34 g). The oxiranemethanol tosylate (0.66 g, 2.0 mmol) of geraniol and the telluride reagent were combined in a mortar and mixed (20 s) before being transferred again to the beaker and microwaving for 9.5 min. After workup, linalool (0.26 g, 1.7 mmol, 83%) was obtained.

2-Methyl-1-phenyl-2-propen-1-ol. Tellurium (0.750 g, 5.88 mmol) was reduced under microwave conditions by rongalite (2.772 g, 17.99 mmol)-KOH (1.00 g, 17.8 mmol),

 $Ca_5(PO_4)_3(OH)$ (1.00 g). The oxiranemethanol tosylate (0.954 g, 2.99 mmol) of 2-methyl-3-phenyl-2-propen-1-ol was sonicated with the telluride mixture for 14 min as described for linalool. The ¹H NMR spectrum indicated a 1:1 mixture of starting material and product.

One-pot Reactions.

The oxiranemethanol tosylate, Te, rongalite, and KOH (molar ratios 1:2:6:6) were mixed in a mortar with a spatula for 20-30 s. The mixture was transferred to a round-bottomed flask (for ultrasonication) or a beaker (for microwave irradiation). Samples were removed every 20 min (ultrasound) or 3 min (microwave) and analyzed by TLC or ¹H NMR spectroscopy. Workups were as previously described.

1-Nonen-3-ol. The product (0.26 g, 1.7 mmol, 90%) was obtained by sonication for 12 h of the oxiranemethanol tosylate (0.627 g, 2.00 mmol) of 2-nonen-1-ol with Te (0.51 g, 4.0 mmol) rongalite (1.849 g, 12.00 mmol) KOH (0.673 g, 12.0 mmol), and Al₂O₃ (1.34 g).

Linalool (With Catalytic Te). The product (0.596 g, 3.86 mmol, 95%) was obtained by sonication for 12 h of a mixture of the oxiranemethanol tosylate (1.301 g, 4.000 mmol), Te (0.255 g, 2.00 mmol), rongalite (3.67 g, 23.8 mmol), KOH (1.347 g, 24.01 mmol) and Al₂O₃ (2.693 g).

Phase Transfer Conditions.

1-Phenyl-2-propen-1-ol. An aqueous suspension (10 mL) of Te (0.76 g, 6.0 mmol) was heated (60 °C) for 2 h under argon with rongalite (2.8 g, 18 mmol) and NaOH (0.72 g, 18 mmol). The original black suspension of Te was transformed into a deep red-purple solution containing telluride ions (Te_n^{2-}). The solution was cooled to room temperature and the quaternary ammonium phase transfer catalyst Adogen 464 (0.17 g) in water (1 mL) and the oxiranemethanol tosylate (0.91 g, 3.0 mmol) of cinnamyl alcohol in toluene (15 mL) were added. Black elemental Te began to precipitate after about 15 min. The mixture was stirred for 2 h, and the layers were allowed to separate. Air may be bubbled through the mixture to facilitate oxidation of excess telluride ions. The toluene layer was removed, dried (MgSO₄), and filtered through a pipet of silica gel to remove Te^o followed by evaporation of the solvent to give nearly pure 1-phenyl-2-propen-1-ol (0.40 g, 3.0 mmol, 98%).

2-Methyl-1-phenyl-2-propen-1-ol (With Catalytic Te). The product (0.42 g, 2.83 mmol, 94%) was obtained as described above from the oxiranemethanol tosylate (0.95 g, 3.0 mmol), Te (0.05 g, 0.34 mmol), rongalite (2.0 g, 13 mmol), NaOH (0.44 g, 11 mmol), and Adogen 464 (0.20 g) except that the mixture was heated to 65 °C and stirred vigorously overnight (12 h). The reaction with excess Te^o (0.76 g, 6.0 mmol) gave a 99% yield of product (0.440 g, 2.97 mmol) from the same amount of starting materials. Without heating this reaction was complete in 2 h.

1-Octen-3-ol. The product (0.36 g, 2.8 mmol, 93%) was obtained as described for 1-phenyl-2-propen-1ol from the oxiranemethanol tosylate (0.9 g, 3 mmol) of 2-octen-1-ol. The procedure for the other allylic alcohols is the same.

1-Nonen-3-ol. The product (0.420 g, 2.95 mmol, 98%) was obtained from the oxiranemethanol tosylate (0.94 g, 3.0 mmol) of 2-nonen-1-ol.

Linalool. The product (0.58 g, 3.8 mmol, 90%) was obtained from the oxiranemethanol tosylate (1.36 g, 4.2 mmol) of geraniol.

Nerolidol. The product (0.64 g, 2.88 mmol, 96%) was obtained from the oxiranemethanol tosylate (1.18 g, 3.00 mmol) of farnesol.

Trituration in a Mortar.

Reduction of Tellurium. Tellurium (1.0 g, 7.8 mmol), rongalite (3.60 g, 23.4 mmol), and KOH (1.30 g, 23.4 mmol) were triturated in a mortar with a pestle (glove bag, N_2) for 5 min at room temperature. (The quantity of Te⁰ varied between 0.9 g and 1.5 g) The mixture was transferred to a flask (100 mL) which was sealed, removed from the glove bag, and heated (85 °C, external temperature, oil bath) for 3 h. After 1 h the mixture became a deep purple color. After a total of 3 h, the telluride mixture was cooled to room temperature and used in reactions with oxiranemethanol tosylates.

General Procedure for "No-Solvent" Reaction of Oxiranemethanol Tosylates with Telluride Ions. The reduced tellurium reagent was transferred to a mortar at room temperature (glove bag, N₂). The oxiranemethanol tosylate was added and mixed with a spatula followed by trituration with a pestle intermittantly for three or four (or more) five-minute periods. The mixture tended to be sticky. The formation of black elemental Te was observed within the first 5 min. After about 30 min. the reaction mixture appeared completely black. The reaction was followed by ¹H NMR spectroscopy, and reactions were essentially complete in 1 h. Workup consisted of addition of water (a few drops) and ether (10 mL) to the mortar followed by trituration

with a pestle. The ether and water were allowed to separate and the ether layer was removed by a pipet. The reaction mixture was extracted further with ether (4x7 mL), the ether extracts were combined, filtered, and dried (MgSO₄). If the extraction of the sticky reaction mixture is not done efficiently, yields will be lower. Careful evaporation of the ether gave almost pure product which can be purified further if necessary by flash chromatography (silica gel, hexanes-ether).

1-Phenyl-2-propen-1-ol. The product (0.380 g, 2.83 mmol, 60%) was obtained along with cinnamyl alcohol (3-phenyl-2-propen-1-ol) from the oxiranemethanol tosylate (1.43 g, 4.70 mmol) of cinnamyl alcohol. When the optically active tosylate of (2*R*, 3*R*)-3-phenyl-2-oxiranemethanol (0.890 g, 7.00 mmol) was used, (*S*)-1-phenyl-2-propen-1-ol was obtained [0.180 g, 1.35 mmol, 45%; $[\alpha]_{D}^{25}$ -0.68 (c 3.5, CHCl₃), lit³⁴ $[\alpha]_{D}^{25}$ -0.66 (c 3.44, CHCl₃)]. Cinnamyl alcohol was a byproduct whose yield of 20% was estimated from ¹H NMR spectra.

2-Methyl-3-phenyl-1-propen-3-ol. The product (0.430 g, 2.90 mmol, 97%) was obtained from the oxiranemethanol tosylate (0.950 g, 3.00 mmol) derived from 2-methyl-3-phenyl-2-propen-1-ol.

1-Octen-3-ol. The product (0.320 g, 2.50 mmol, 83%) was obtained from the oxiranemethanol tosylate (0.900 g, 3.00 mmol) derived from 2-octen-1-ol.

1-Nonen-3-ol. The product (0.390 g, 2.70 mmol, 95%) was obtained from the oxiranemethanol tosylate (0.900 g, 2.87 mmol) derived from 2-nonen-1-ol.

Linalool. The product (0.360 g, 2.33 mmol, 76%) was obtained from the oxiranemethanol tosylate (1.00 g, 3.08 mmol) derived from geraniol.

Nerolidol. The product (0.640 g, 2.88 mmol, 96%) was obtained from the oxiranemethanol tosylate (1.18 g, 3.00 mmol) of farnesol.

2-Methylenecyclohexanol. The product (0.340 g, 3.04 mmol, 87%) was obtained from the tosylate of 7oxabicyclo[4.1.0] heptane-1-methanol (1.00 g, 3.50 mmol).

l-Hepten-3-ol. The product (0.350 g, 2.73 mmol, 91%) was obtained from the tosylate of α -*n*-butyloxiranemethanol (0.900 g, 3.00 mmol).

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