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

Qinyu Xu, Bin Chao, Yongmei Wang, and Donald C. Dittmer*

Room 1-014 CST, Department of Chemistry, Syracuse University,
Syracuse, New York 13244, USA

Abstract: Elemental tellurium can be reduced by rongalite ($HOCH_2SO_2Na\cdot2H_2O$)-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-toxic[1] 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 substrates[4] 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^0 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]

$$Te^0 \xrightarrow{\text{reducing agent}} Te^{2-} \xrightarrow{\text{substrate}} \text{product} + Te^0$$
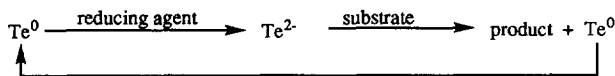
Scheme 1. The Nucleophilic Reduction Process.

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.

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 (SOCl$_2$, NaIO$_4$, RuCl$_3$·3H$_2$O).[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]

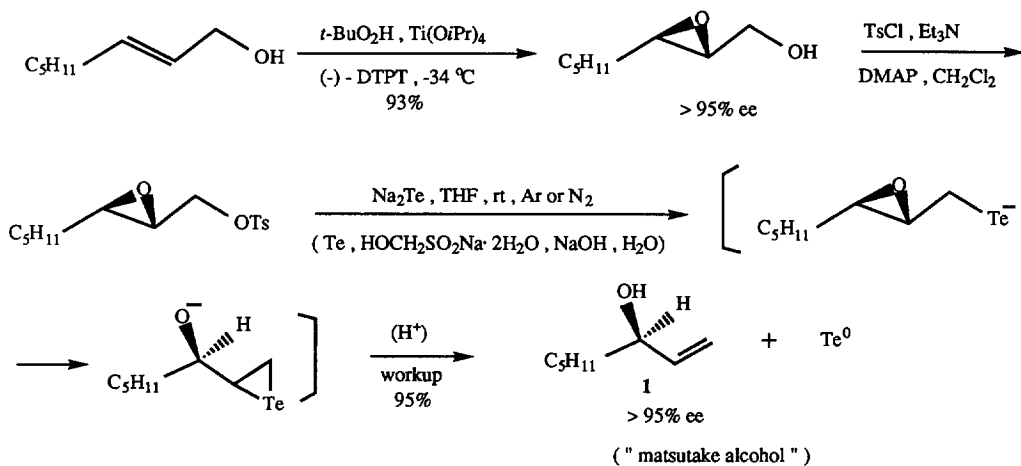$$BrCH_2CH_2Br + Te^{2-} \longrightarrow CH_2 = CH_2 + Te^0 \qquad (1)$$
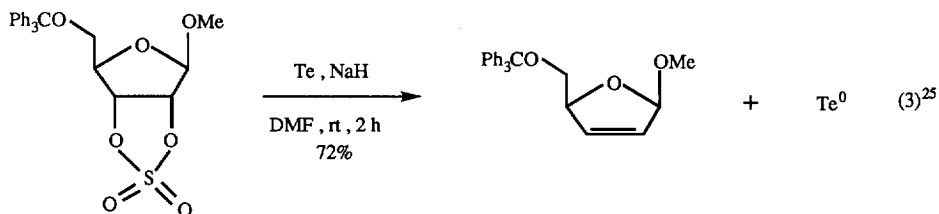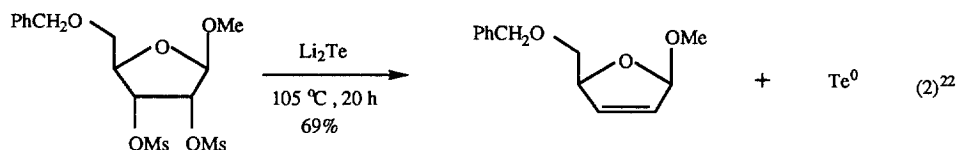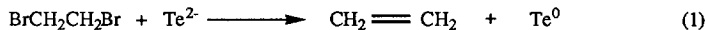
Allylic Alcohols

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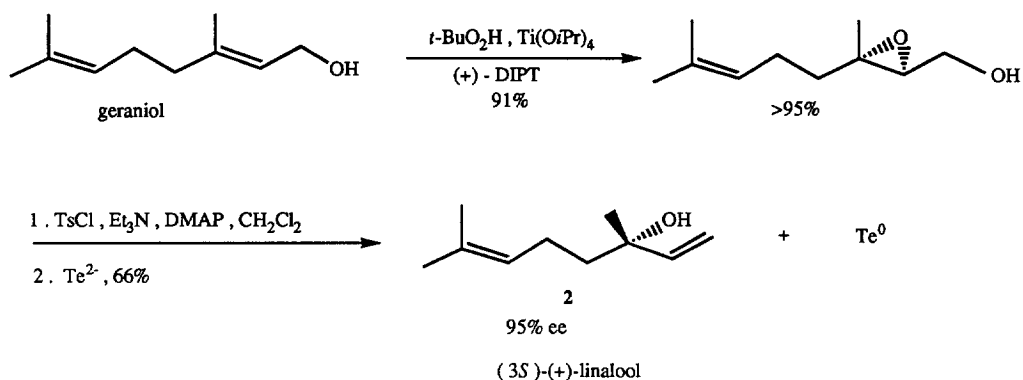
epoxidation that occurs with a monosubstituted double bond when attempting to resolve racemic **1** or **3**. A putative mechanism that is applicable to other schemes is included in Scheme 3 .
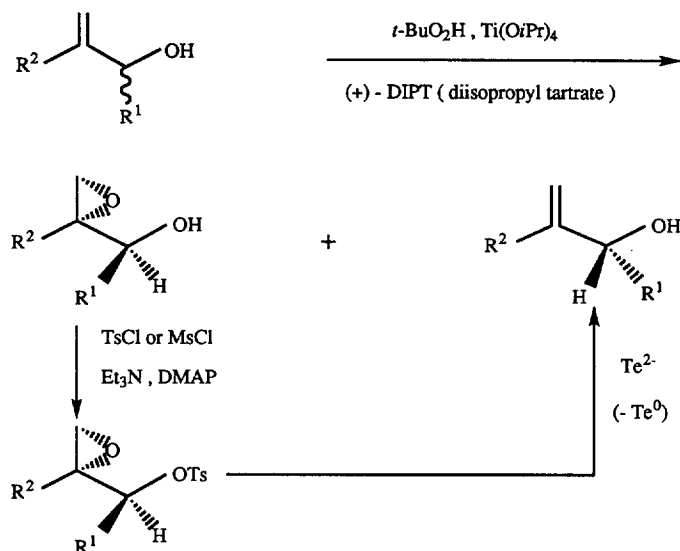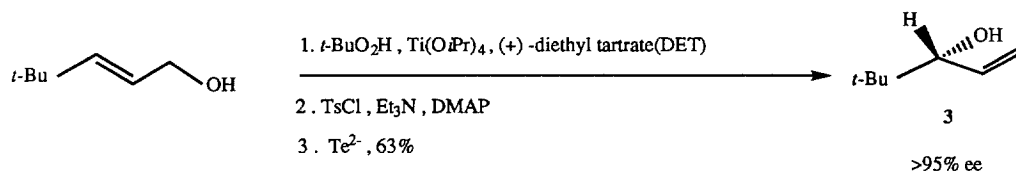

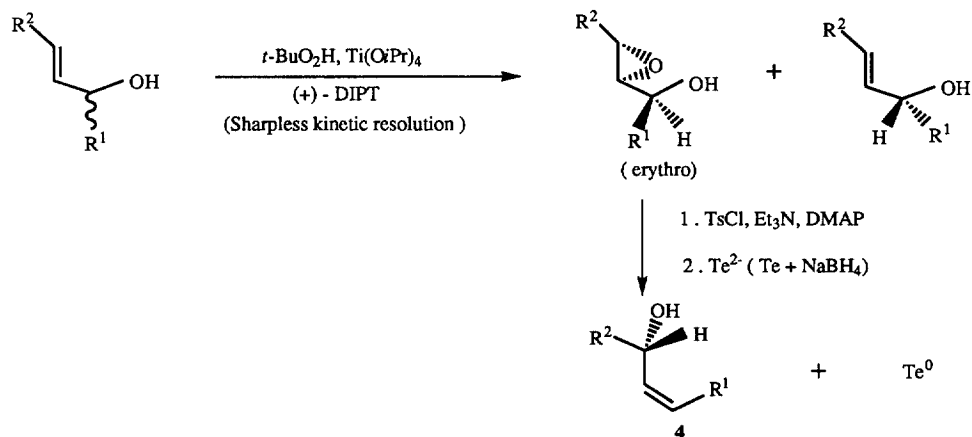**Scheme 2.** Avoidance of the 50% Limitation in the Kinetic Resolution of a Secondary Allylic Alcohol (Method 1).

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

geraniol

t-BuO$_2$H , Ti(O*i*Pr)$_4$

(+) - DIPT

91%

>95%

1 . TsCl , Et$_3$N , DMAP , CH$_2$Cl$_2$

2 . Te^{2-} , 66%

+   Te^0

2

95% ee

(3*S*)-(+)-linalool

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

t-Bu   OH

1. *t*-BuO$_2$H , Ti(O*i*Pr)$_4$, (+) -diethyl tartrate(DET)

2 . TsCl , Et$_3$N , DMAP

3 . Te^{2-} , 63%

t-Bu   **3**

>95% ee

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**).

R^2 OH   R^1

t-BuO$_2$H, Ti(O*i*Pr)$_4$

(+) - DIPT

(Sharpless kinetic resolution)

R^2 O   OH   R^1 H

(erythro)

+   R^2 OH   H   R^1

1 . TsCl, Et$_3$N, DMAP

2 . Te^{2-} (Te + NaBH$_4$)

R^2 OH   H   R^1

4

+   Te^0

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 precursor[35]), (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]
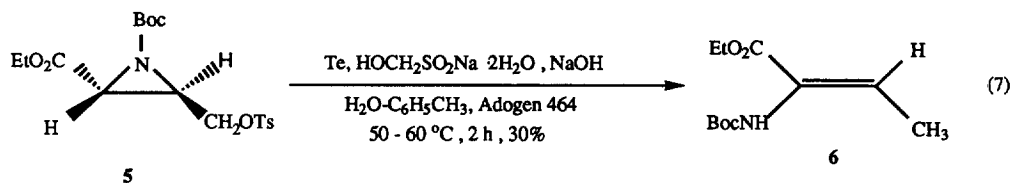
The tellurium procedure has been adapted for use with as little as 10 mol % of telluride ion in conjunction with excess reducing agent.[39] In this way (S)-(+)-linalool is obtained in 97% yield from (2S, 3S)-epoxygeraniol tosylate in aqueous THF.

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 (HOCH$_2$SO$_2$Na•2H$_2$O) 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 byproduct[36] is acting as a mild Lewis acid catalyst.
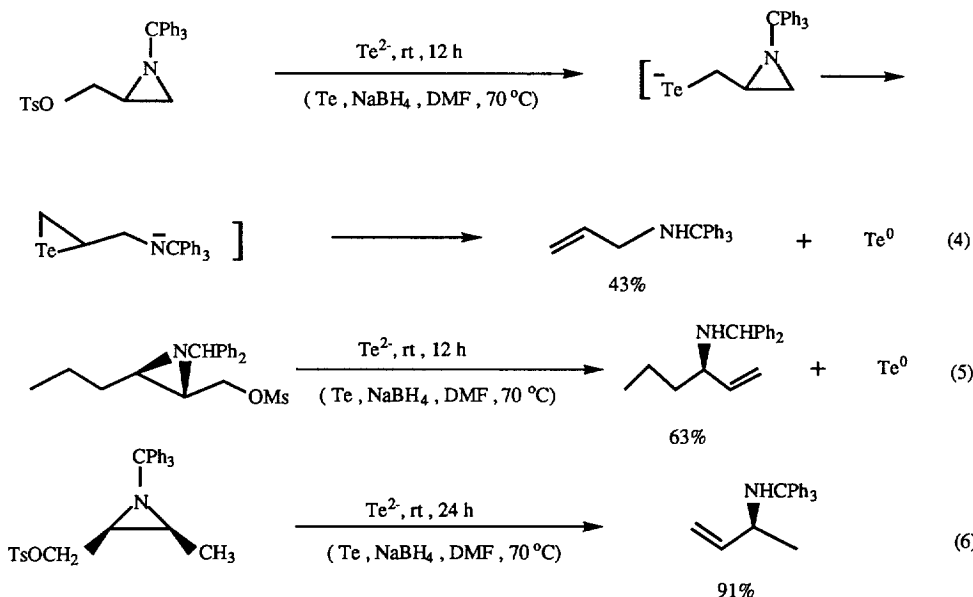
Aziridine 5 with an electron-withdrawing *t*-butoxycarbonyl (Boc) substituent on nitrogen yielded under phase-transfer conditions an isomerized product 6, analogous to the isomerization of a vinylglycine derivative reported by Rapoport and Afzali-Ardakani.[42]

$$\text{5} \xrightarrow[\begin{subarray}{c} H_2O\text{-}C_6H_5CH_3,\ \text{Adogen 464} \\ 50\text{ - }60\,^\circ C\,,\,2\,h\,,\,30\% \end{subarray}]{\text{Te, HOCH}_2\text{SO}_2\text{Na 2H}_2\text{O , NaOH}} \text{6} \qquad (7)$$

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 eliminated[43]. 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, $HOCH_2SO_2Na\cdot2H_2O$, and KOH in a mortar in an inert atmosphere (Ar or N_2).[44] This initial process has been improved (1) by the addition of alumina, 4A molecular sieves, TiO_2, or hydroxyapatite [$Ca_5(PO_4)_3OH$] 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 bath[45] 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 ^{1}H 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.
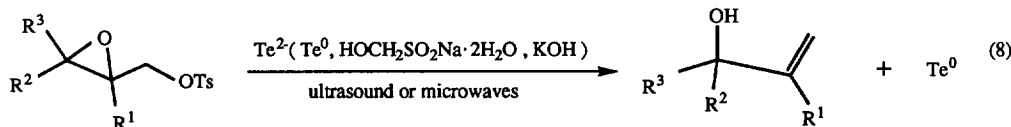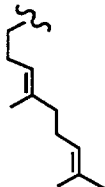
$$\xrightarrow[\text{ultrasound or microwaves}]{\text{Te}^{2-}(\text{ Te}^0,\ \text{HOCH}_2\text{SO}_2\text{Na}\cdot2\text{H}_2\text{O , KOH })} \qquad +\quad \text{Te}^0 \qquad (8)$$

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

Entry	R^1	R^2	R^3	Conditions	t, min	Yield, % (isolated)
1	H	$n\text{-}C_5H_{11}$	H	Al_2O_3[a]	150	> 95
2	H	$n\text{-}C_6H_{13}$	H	Al_2O_3[a]	720	90 [b]
3	CH_3	Ph	H	tartaric acid[a]	60	85
4	CH_3	Ph	H	c	14	50[d,e]
5	H	(prenyl chain)	CH_3	Al_2O_3[a]	120	86[f]
6	H	(prenyl chain)	CH_3	c	9.5	83
7	H	(farnesyl chain)	CH_3	Al_2O_3[a]	360	89

a) Ultrasonic bath . b) One-pot reaction. c) Microwave, 525 W. d) Reaction was interrupted before completion.
e) Yield by ^{1}H 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 microwaves[46].
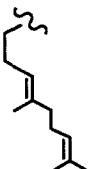
A one-pot procedure shows promise. In this method all reagents (substrate, Te^0, rongalite, and KOH) are mixed and ultrasonicated. The telluride reacts with the neat oxiranemethanol tosylate as the former is produced

by reduction of Te^0. Since the elemental Te^0 that is extruded during the reaction is more finely divided than the original 200 mesh Te^0, 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^0 is reduced in aqueous rongalite-NaOH at 60 °C under argon to give a deep red-purple 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^0 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	H	Ph	H	97
2	CH_3	Ph	H	99[a]
3	H	$n\text{-}C_5H_{11}$	H	93
4	H	$n\text{-}C_6H_{13}$	H	98
5	H		CH_3	90
6	H		CH_3	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 Te^0, rongalite, and KOH in a mortar (glove bag, N_2 or Ar), transferal of the mixture to a flask, and heating of the sealed flask outside of the glove bag (80 °C) for 3 h gave a purple telluride mixture.

The sticky telluride reagent and oxiranemethanol tosylate were triturated together in a mortar (glove bag, N_2 or Ar) periodically for about an hour, black Te^0 being observed within 5 min. Table 3 shows the results. In addition to the tosylates of primary oxiranemethanols, a secondary substrate, **7**, als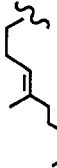o performed well (Eq. 9) as did a cyclic substrate (Entry 7). Epoxyditosylate **8** also reacted and the ^1H NMR spectrum of the product is consistent with the formation of butadiene monoxide (Eq. 10). An isolated yield has not yet been obtained because of the volatility of the product.

$$n\text{-Bu} \overset{OTs}{\diagup\!\!\diagdown}\!\!\diagdown\!\!O \xrightarrow{Te^{2-}} n\text{-Bu}\overset{OTs}{\diagup\!\!\diagdown}\!\!\diagdown \quad + \quad Te^0 \qquad (9)$$

7   91%

$$TsO\diagdown\!\!\diagup\!\!\diagdown\!\!O\!\!\diagdown\!\!\diagup OTs \xrightarrow{Te^{2-}} O\diagdown\!\!\diagup\!\!\diagdown\!\!\diagdown \quad + \quad Te^0 \qquad (10)$$

8
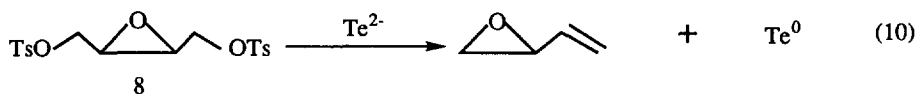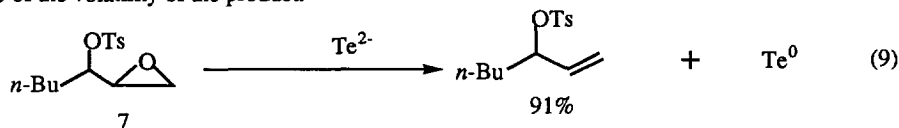
We now prefer the techniques involving ultrasound, microwave, or phase-transfer catalysis to the mortar and pestle method because the former are more reliable. One trituration experiment in the mortar is not always reproduced by the next, and the variable stickiness of the reaction mixture is a drawback.

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

Entry	R^1	R^2	R^3	Yield, % (isolated)
1	H	Ph	H	60 [a,b]
2	CH_3	Ph	H	97
3	H	$n\text{-}C_5H_{11}$	H	83
4	H	$n\text{-}C_6H_{13}$	H	95
5	H	(isoprenyl chain)	CH_3	76
6	H	(terpenyl chain)	CH_3	96
7	$-(CH_2)_4-$		H	87

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 Te^0), 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 Te^{2-} and that a relatively low energy pathway exists for the extrusion of elemental tellurium.

EXPERIMENTAL SECTION

All reactions were performed under an inert atmosphere (N_2 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 Al_2O_3 (Grade I), TiO_2, or $Ca_5(PO_4)_3(OH)$ 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 acid[34] 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 oven[48]. ^{1}H NMR spectra were taken at 300 MHz in $CDCl_3$.

General Procedure for Reduction of Te^0 Under Ultrasonication.

Tellurium (1.021 g, 7.990 mmol, or 1 equiv), KOH-Al_2O_3 (4.04 g; 24.00 mmol KOH, or 3 equiv) and rongalite ($HOCH_2SO_2Na\cdot 2H_2O$) (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 N_2. Ultrasonication for 2-3 h resulted in a red-purple solid (Te_n^{-2}). The same procedure was used for TiO_2, $Ca_5(PO_4)_3(OH)$, and 4A molecular sieves.

General Procedure for Reduction of Te^0 Under Microwave Irradiation.

Tellurium (0.51 g, 4.0 mmol), KOH-Al_2O_3 (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 N_2 (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 $Ca_5(PO_4)_3(OH)$.

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^0 was reduced and was sealed under N_2. During sonication small samples were removed and analyzed by ^{1}H 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^0 and insoluble inorganic substances and dried

(Na$_2$SO$_4$ or MgSO$_4$). 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 Te^{2-} (2 equiv) as described above. The reaction mixture was transferred to the beaker (50 mL) in which the Te^o was reduced, the contents of the beaker under N$_2$ were sealed with plastic wrap and microwaved. A sample was withdrawn every 3-4 min and analyzed by TLC or ^{1}H 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)-Al$_2$O$_3$(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 ^{1}H 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 ^{1}H 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 Al$_2$O$_3$ (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 Al$_2$O$_3$ (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° 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° (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-1-ol 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, N₂) for 5 min at room temperature. (The quantity of Te° 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 (MgSO$_4$). 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%; [α]$_D^{25}$ -0.68 (c 3.5, CHCl$_3$), lit[34] [α]$_D^{25}$ -0.66 (c 3.44, CHCl$_3$)]. Cinnamyl alcohol was a byproduct whose yield of 20% was estimated from ^{1}H 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 7-oxabicyclo[4.1.0] heptane-1-methanol (1.00 g, 3.50 mmol).

1-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).

REFERENCES AND NOTES

1. (a) Lewis, R.J. Sr., *Sax's Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold: New York, 1996, Vol. III, TAJ 500, p. 3068. "Elemental tellurium has relatively low toxicity." (b) Sittig, M., *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, 2nd ed., Noyes: Park Ridge, NJ, 1985, pp. 828-829. "The toxicity of tellurium and its compounds is of low order. There is no indication that either tellurium dust or fume is damaging to the skin or lungs." (c) Cooper, W.C., *Tellurium*, Van Nostrand Reinhold: NY, 1971, pp. 313-321. "In view of the fact that there are a number of misconceptions regarding the toxicity of tellurium and its compounds, it is appropriate to present data on this subject----. Tellurium has not been found to be a very hazardous element in industrial use, although it can cause a pronounced garlic odor of the breath----. The maximum concentration of tellurium in the air at which no garlic breath appears is given as 0.01 to 0.02 mg of tellurium per cubic meter of air." (d) Elemental tellurium has been removed from the Superfund list since it does not meet the criteria for hazardous substances, *C&EN* Oct. 17, 1994, p. 38. (e) In our process tellurium is not consumed and we have not detected any tellurium containing products except for tellurophenes: Discordia, R.P.;

Dittmer, D.C. *Tetrahedron Lett.* **1988**, *29*, 4923-4926. Removal of tellurium, especially in catalytic amounts, is easy to do by filtration, centrifugation, or flotation. (See references 34a and 39).

2. *Aldrich Chemical Co. Catalog*, **1996-97**, p 1364.

3. A variety of reducing agents have been used: eg $HOCH_2SO_2N_a \cdot 2H_2O$ (rongalite), $NaBH_4$, $LiEt_3BH$, Na, $NaC_{10}H_8$, NaH). For reviews on tellurium chemistry see: (a) Petragnani, N. *Tellurium in Organic Synthesis*, Academic Press: London, 1994. (b) Irgolic, K.J., *Methods of Organic Chemistry (Houben-Weyl). Organotellurium Compounds*, Klamann, D., Ed.; G. Thieme: Stuttgart, 1990, Vol. E, 12b. (c) Petragnani, N.; Comasseto, J.V. *Synthesis* **1991**, 793-817, 897-919. (d) Dittmer, D.C. *Encyclopedia of Reagents for Organic Synthesis*, Paquette, L., Ed.; Wiley: Chichester, 1995, Vol 7, pp 4628-4631. (e) Dittmer, D.C. *Encyclopedia of Reagents for Organic Synthesis*, Paquette, L., Ed.; Wiley: Chichester, 1995, Vol 4, pp 2749-2750. (f) *The Chemistry of Organic Selenium and Tellurium Compounds*, Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1986, Vol. 1. (g) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: Chichester, 1987, Vol. 2. (h) Sadekov, I.D.; Rivkin, B.B.; Minkin, V.I. *Russ. Chem. Rev.* **1987**, *56*, 586-608. (i) Engman, L. *Phosphorus Sulfur* **1988**, *38*, 105-119.

4. The nucleophilicity of Te^{2-} has not been determined; it should be high because of the trend in the chalcogen nucleophiles, n_{CH_3I} (PhO^-, 5.75; PhS^-, 9.92; $PhSe^-$, ~10.7): Pearson, R.G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319-326.

5. The standard reduction potential for $Te^o \rightarrow Te^{2-}$ is -1.14 V in a basic medium: Greenwood, N.N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, 1984, pp 890-896. For example, hydrogen telluride is a strong reducing agent and oxidizes very rapidly in air to Te^o: *Tellur. Gmelins Handbuch Der Anorganischen Chemie*, 8th ed.; Hantke, G., Ed.; Springer: Berlin, 1976, Suppl. Vol. B1, pp 1-12. See also ref. 3e.

6. Björgvinsson, M.; Schrobilgen, G.J. *Inorg. Chem.* **1991**, *30*, 2540-2547.

7. Farrar, W.V.; Gulland, J.M. *J. Chem. Soc.* **1945**, 11-14.

8. Barton, D.H.R.; McCombie, S.W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574-1585.

9. Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 1009.

10. Osuka, A.; Suzuki, H. *Chem. Lett.* **1983**, 119-120.

11. Osuka, A.; Taka-Oka, K.; Suzuki, H. *Chem. Lett.* **1984**, 271-272.

12. Osuka, A.; Takechi, K.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 303-304.

13. Barton, D.H.R.; Fekih, A.; Lusinchi, X. *Tetrahedron Lett.* **1985**, *26*, 3693-3696.

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

15. Suzuki, H.; Inouye, M. *Chem. Lett.* **1986**, 403-406.

16. Padmanabhan, S.; Ogawa, T.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1358-1360.

17. Zhou, X.-J.; Huang, Z.-Z. *Synth. Commun.* **1989**, *19*, 1347-1349.

18. Suzuki, H.; Padmanabhan, S.; Ogawa, T. *Chem. Lett.* **1989**, 1017-1020.

19. Lue, P.; Fan, W.-Q.; Zhou, X.-J. *Synthesis* **1989**, 692-693.

20. Huang, S.; Pi, J.-H. *Synth. Commun.* **1990**, *20*, 2297-2300.

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

22. Clive, D.L.J.; Wickens, P.L. *J. Chem. Soc., Chem. Commun.* **1993**, 923-924. See also the following reference.

23. Bargues, V.; Blay, G.; Fernandez, I.; Pedro, J.R. *Synlett* **1996**, 655-656.

24. Suzuki, H.; Nakamura, T. *J. Org. Chem.* **1993**, *58*, 241-244.

25. Chao, B.; McNulty, K.C., Dittmer, D.C. *Tetrahedron Lett.* **1995**, *36*, 7209-7212.

26. (a) Gao, Y.; Sharpless, K.B. *J. Am. Chem. Soc.* **1988**, *110*, 7538-7539. (b) Reviewed by Lohray, B.B. *Synthesis* **1992**, 1035-1052.

27. Beels, C.M.D.; Coleman, M.J.; Taylor, R.J.K. *Synlett* **1990**, 479-480.

28. Santoyo-González, F.; Garcia-Calvo-Flores, F.; Garcia-Mendoza, P.; Hernandez-Mateo, F.; Isac-Garcia, J.; Pérez-Alvarez, D. *J. Chem. Soc., Chem. Commun.* **1995**, 461-462.

29. Chan, T.H.; Finkenbine, J.R. *Tetrahedron Lett.* **1974**, 2091-2094.

30. (a) Tan, R.P.-K.; Gillette, G.R.; Powell, D.R.; West, R. *Organometallics* **1991**, *10*, 546-551. (b) Tsumuraya, T.; Kabe, Y.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1990**, 1159-1160. (c) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 834-835.

31. (a) Bäckvall, J.-E.; Engman, L. *Tetrahedron Lett.* **1981**, *22*, 1919-1922. (b) Clive, D.L.J.; Beaulieu, P.L. *J. Org. Chem.* **1982**, *47*, 1124-1126. (c) Connor, J.; Greig, G.; Strausz, O.P. *J. Am. Chem. Soc.* **1969**, *91*, 5695-5696.

32. Reviewed by (a) Johnson, R.A.; Sharpless, K.B. *Comprehensive Organic Chemistry*, Trost, B.M., Ed.; Pergamon Press: Oxford, 1991, Vol. 7, Chapt. 3.2. (b) Katsuki, T.; Martin, V.S. *Org. React.* **1996**, *48*, 1-299.

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

34. (a) Dittmer, D.C.; Discordia, R.P.; Zhang, Y.; Murphy, C.K.; Kumar, A.; Pepito, A.S.; Wang, Y. *J. Org. Chem.* **1993**, *58*, 718-731. (b) Discordia, R.P.; Dittmer, D.C. *J. Org. Chem.* **1990**, *55*, 1414-1415. (c) Discordia, R.P.; Murphy, C.K.; Dittmer, D.C. *Tetrahedron Lett.* **1990**, *31*, 5603-5606. (d) Treatment of glycidyl acetates with telluride ion, unlike tosylates and mesylates, results in deoxy-genation and deacetylation. A by-product of the reduction of tellurium, triethylborane, is believed to be involved in the reactions of these acetates: Dittmer, D.C.; Zhang, Y.; Discordia, R.P. *J. Org. Chem.*, **1994**, *59*, 1004-1010.

35. Barner, R.; Hübscher, J. *Helv. Chim. Acta* **1983**, *66*, 880-890.

36. Kumar, A.; Dittmer, D.C. *J. Org. Chem.* **1994**, *59*, 4760-4764.

37. Pepito, A.S.; Dittmer, D.C. *J. Org. Chem.* **1994**, *59*, 4311-4312.

38. Roush, W.R.; Brown, R.J. *J. Org. Chem.* **1983**, *48*, 5093-5101.

39. Kumar, A.; Dittmer, D.C. *Tetrahedron Lett.* **1994**, *35*, 5583-5586.

40. (a) A report on preliminary results: Pepito, A.S.; Dittmer, D.C. *Abstracts, 209th National Meeting, Am. Chem. Soc.*, Anaheim, CA, April 2-6, 1995, ORGN 023. (b) Pepito, A.S.; Dittmer, D.C. *J. Org. Chem.* **1997**, submitted. (c) Pepito, A.S. *Nucleophilic Reductions of Sulfonate Esters of Oxiranemethanols and Aziridinemethanols by the Telluride Ion to Give Allylic Alcohols and Allylic Amines*, Syracuse University, 1996.

41.   (a) Gonda, J.; Helland, A.-C.; Ernst, B.; Bellus, D. *Synthesis* **1993**, 729-733. (b) Hayashi, T.;
       Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J Am. Chem. Soc.* **1989**, *111*, 6301-
       6311. (c) Alcón, M.; Canas,M.; Poch, M.; Moyano, A.; Pericás, M.A.; Riera, A. *Tetrahedron Lett.*
       1994, *35*, 1589-1592. (d) Burgess, K.; Liu, L.T.; Pal, B. *J. Org. Chem.* **1993**, *58*, 4758-4763. (e)
       Bower,J.F.; Williams, J.M.J. *Synlett* **1996**, 685-686. (f) Jumnah, R.; Williams, A.C.; Williams,
       J.M.J. *Synlett* **1996**, 821-822. (g) Berkowitz, D.R.; Pumphrey, J.A.; Shen, Q. *Tetrahedron Lett.*
       1994, *47*, 8743-8746. (h) Duthaler, R.O. *Tetrahedron* **1994**, *50*, 1539-1650.

42.   Afzali-Ardakani, A.; Rapoport, H. *J. Org. Chem.* **1980**, *45*, 4817-4820.

43.   For reviews of organic reactions performed in the solid phase see (a) Toda, F. *Acc. Chem. Res.* **1995**,
       28, 480-486. (b) Toda, F. *Synlett* **1993**, 303-312. (c) Toda, F., *J. Synth. Org. Chem. Jpn.* **1994**,
       52, 923-934. (d) Singh, N.B.; Singh, R.J.; Singh, N.P. *Tetrahedron* **1994**, *50*, 6441-6493. (e)
       McBride, J.M.; Segmuller, B.E.; Hollingsworth, M.D.; Mills, D.E.; Weber, B.A. *Science* **1986**, *234*,
       830-835. (f) Paul, I.C.; Curtin, D.Y. *Acc. Chem. Res* **1973**, *6*, 217-225. (g) Cohen, M.D.; Green,
       B.S. *Chem. Br.* **1973**, *9*, 490-497. (h) Morawetz, H. *Science* **1966**, *152*, 705-711.

44.   Wang, Y.; Dittmer, D.C. *Abstracts, 211th National Meeting, Am. Chem. Soc.*, New Orleans, LA,
       March 24-28, 1996, ORGN 430. (See also *Chem. Eng. News*, **1996**, April 8, pp 43-44.)

45.   For reviews of the uses of ultrasound see (a) Suslick, K.S. *Ultrasound: Its Chemical, Physical, and
       Biological Effects*, VCH: New York, 1988. (b) Suslick, K. *Science*, **1990**, *247*, 1439-1445. (c)
       Price, G.J., Ed. *Current Trends in Sonochemistry*, Royal Society of Chemistry: Cambridge, **1992**. (d)
       Ley, S.V.; Low, C.M.R. *Ultrasound in Synthesis*, Springer-Verlag: Berlin, 1989. (e) Pestman, J. M;
       Engberts, J.B.F.N.; De Jong, F. *Recl. Trav. Chim. Pays-Bas* **1994** , *113*, 533-542. (f) Lindley, J.;
       Mason, T. J. *Chem. Soc. Rev.* **1987**, *16*, 275-311.

46.   For reviews on the use of microwaves in organic chemistry see (a) Caddick, S. *Tetrahedron* **1995**, *51*,
       10403-10432. (b) Bose, A. K.; Manhas, M. S.; Ghosh, M.; Shah, M.; Raju, V.S.; Bari, S.S.; Newaz,
       S. N.; Banik, B.K.; Chaudhary, A.G.; Barakat, K.J. *J. Org. Chem.* **1991**, *56*, 6968-6970. (c)
       Mingos, D.M.P.; Baghurst, D.R. *Chem. Soc. Rev.* **1991**, *20*, 1-47. (d) Majetich, G.; Hicks, R.
       Radiat. Phys. Chem. **1995**, *45*, 567-579.

47.   (a) Sharpless, K.B.; Verhoeven, T.R. *Aldrichim Acta* **1979**, *12*, 63-74. (b) Sharpless, K.B.;
       Michaelson, R.C. *J. Am. Chem. Soc.* **1973**, *95*, 6136-6137.

48.   We are grateful to Eugene Polyak who determined the power of the microwave oven as 525 W
       according to Watkins, K.W. *J. Chem. Ed.* **1983**, *60*, 1043-1044.