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A Catalytic Tellurium Process for the Transposition of Allylic Hydroxyl Groups and Carbon-Carbon Double Bonds

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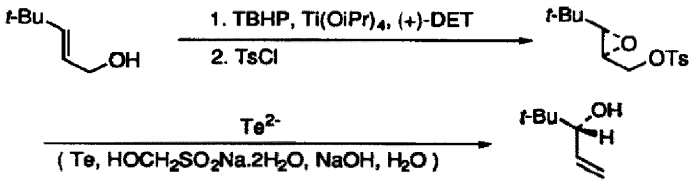
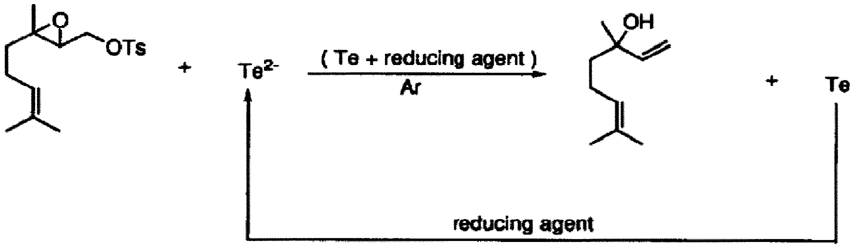
Abstract: As little as 0.1 molar equivalent of elemental tellurium in combination with excess (up to 3 molar equivalents) reducing agent ($HOCH_2SO_2Na•2H_2O$, $NaBH_4$, or $LiEt_3BH$) effects the telluride-ion mediated transposition of allylic hydroxyl groups and carbon-carbon double bonds that proceeds *via* the epoxy tosylate. The workup is much more convenient than when a molar equivalent of tellurium is used.

Introduction. Telluride ion (Te^{2-}) previously has been used in stoichiometric amounts or greater in the conversion of glycidyl tosylates or mesylates to allylic alcohols, a process whose end result is the transposition of an allylic alcohol group and the carbon-carbon double bond.[1] The telluride anion is converted to elemental Te during the reaction. The glycidol derivatives may be obtained optically active *via* the Sharpless asymmetric epoxidation and kinetic resolution procedures that involve *t*-butyl hydroperoxide, titanium isopropoxide, and an optically pure tartrate ester such as diisopropyl tartrate or diethyl tartrate (DET).[2] The Te-transposition coupled with asymmetric epoxidation enables the chemist to overcome several limitations of the Sharpless synthesis of optically active allylic alcohols.[1] These are (1) the inability to resolve tertiary allylic alcohols; (2) the 50% yield limitation in a resolution of secondary allylic alcohols[3]; (3) the poor yields and enantiomeric excess (ee) of sterically congested *trans*, secondary allylic alcohols (eg *t*-butyl vinyl carbinols); (4) the slow epoxidation of monosubstituted carbon-carbon double bonds in allylic alcohols; and (5) the low ee in attempts to resolve *cis*-allylic alcohols that have bulky cis substituents.[2] Advantages of the Te process over other methods are (1) the recovery and reuse of the elemental tellurium; (2) the use of mild temperatures; and (3) with rongalite ($HOCH_2SO_2Na•2H_2O$) as the *in situ* reducing agent for Te, the use of a highly aqueous medium that minimizes the disposal or recovery of large amounts of organic solvent. In addition, elemental Te is relatively non-toxic.[4] A common alternative method of transposition which has been applied on a 32 to 62 millimolar scale[5] consists of treatment of the epoxy tosylates with a zinc-copper couple and sodium iodide in THF or ethylene glycol at elevated temperatures. The zinc-copper couple is consumed in stoichiometric quantities. This and other methods have been discussed in our earlier paper.[1] Equation 1 exemplifies the tellurium process as applied to the synthesis of an optically active *t*-butyl allylic carbinol.[1]

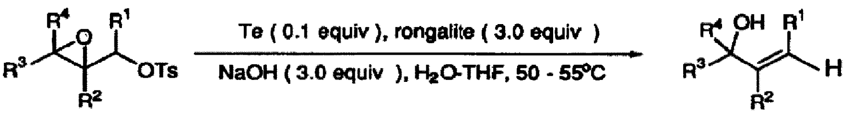


(1)

Catalytic Te Process. While the use of one or more molar equivalents of Te per molar equivalent of epoxy tosylate is satisfactory, the removal of the precipitated Te is tedious on a large scale because of the fineness of the particles. Decreasing the amount of Te has two advantages and one disadvantage. The advantages are the ease of workup and elimination of the need for a significant initial investment in Te. The disadvantage is that the rate of the bimolecular reaction with Te^{2-} is reduced. This latter problem is not serious as shown in Tables 1 and 2 for the reactions of epoxygeranyl tosylate (eq 2) and several other epoxy tosylates (eq 3), respectively.[6] Increasing the temperature of an already facile reaction is all that is needed to give satisfactory yields. If $LiEt_3BH$ is used as the reducing agent for Te, it and the epoxy tosylate are added sequentially and alternately in 5-10 portions to the Te in the reaction flask. This avoids the possibility of reduction of the tosylate by excess $LiEt_3BH$ which has powerful nucleophilic properties.[7] One advantage of the use of $LiEt_3BH$ (Entries 8, 9; Table 1) or $NaBH_4$ (Entry 3, Table 2) is that Lewis acids, Et_3B and Li^+ or BH_3, that may be present from the reduction of Te to Li_2Te or Na_2Te can accelerate the reaction by associating with oxygen atoms in the epoxy tosylates.[1, 8] For reductions of Te by rongalite, an excess of the latter is present at all times so that the elemental Te is reduced rapidly as it is formed. An example of a previous use of catalytic amounts of Te with excess rongalite is the reduction of aromatic nitro compounds to amines.[9] The synthesis of linalool (Table 1) has been done on a scale from 3.1 to 47.2 mmol. The first entry in Table 1 is for the use of a stoichiometric excess of Te at room temperature. The catalytic reactions were slow at room temperature except when reduction of Te was performed with a boron hydride.



(2)



(3)

Table 1. Conversion of Epoxygeraniol Tosylate to Linalool by Catalytic Te^{2-}

Entry	Tosylate, mmol	Reducing Agent[a](mmol)	Te, mmol	Temp, °C[b]	Time, h	yield, %
1	3.08	rongalite, NaOH (18.5, 18.5)	6.2	rt	3.5	88
2	3.08	rongalite, NaOH (9.2, 9.2)	1.2	50-55	2	89
3	3.08	rongalite, NaOH (9.2, 9.2)	0.62	50-55	1	89
4	3.08	rongalite, NaOH (9.25, 9.35)	0.31	50-55	12	92
5	3.08	rongalite, NaOH (9.2, 9.2)	0.31	50-55	12	90[c]
6	20.6	rongalite, NaOH (62.0, 62.0)	2.17	50-55	5	92
7	47.2	rongalite, NaOH (142, 142)	4.77	50-55	3	97[c]
8	3.08	$LiEt_3BH$ (6.78)	0.62	rt	3	84
9	3.08	$LiEt_3BH$ (6.78)	0.31	rt	3	84

(a) Purple solutions containing polytelluride ions, $(Te)_n^{2-}$, are commonly observed. (b) Temperature is external. (c) The tosylate of the (2*S*, 3*S*)-epoxy alcohol was used to give (*S*)-(+)-linalool: $[\alpha]_D^{22}$ +16.94° (*c* 2.12, $CHCl_3$) (Entry 5) ;+17.4° (*c* 5.30, $CHCl_3$) , +17.01° (neat) (Entry 7), ≥ 90% ee [chiral shift reagent, $Eu(hfc)_3$]. Lit $[\alpha]_D^{23}$ (*R*)(-)-linalool, -17.04° (neat), 94-96% ee (shift reagent).[10]

Table 2. Transposition of Other Epoxy Tosylates by Catalytic Te^{2-} (0.1 Molar Equiv)

Entry	R^1	R^2	R^3	R^4	Tosylate, mmol (°C)	Time	Yield,%
1	H	H	n-C_5H_{11}	H	1.37 (50)	2 h	80[a]
2	H	$-(CH_2)_4-$		H	2.39 (50)	12 h	65[b]
3	Me	H	n-C_5H_{11}	Me	0.76 (70)	10 min	87[c, d]

(a) $[\alpha]_D^{23}$ -18.7° (*c* 2.53, EtOH). (b) Low yield due to inadvertent loss of volatile product. $[\alpha]_D^{22}$ +10.6° (*c* 1.76, $CHCl_3$). (c) $NaBH_4$ (2.4 equiv) in DMF was used instead of $HOCH_2SO_2Na \cdot 2H_2O$-NaOH-H_2O-THF. (d) Product is cis.

Experimental. Geraniol (10.1 g, 64.3 mmol) was epoxidized according to the procedure of Sharpless[2b] with (+)-DIPT as the chiral ligand to give (2*S*, 3*S*)-epoxy geraniol (9.40 g, 55.2 mmol, 86%): $[\alpha]_D^{22} = -5.1°$ (*c* 2.73, $CHCl_3$) [lit[2b] $[\alpha]_D^{25}$ -5.3° (*c* 3.0, $CHCl_3$)]. Treatment of the epoxygeraniol (8.20 g, 48.2 mmol) with *p*-toluenesulfonyl chloride[1] (9.68 g, 50.3 mmol) gave an essentially quantitative yield of the tosylate as a yellow oil (16.3 g, slightly contaminated with impurities). A portion of the tosylate (1.0 g, 3.1 mmol) was purified by flash chromatography on silica gel (5:1 pentane/ether) to a pale yellow oil (0.80 g, 2.5 mmol): $[\alpha]_D^{22}$ -19.85° (*c* 5.91, $CHCl_3$); [lit[1] $[\alpha]_D^{25}$ -17.1° (*c* 3.4, $CHCl_3$)]. The remainder of the crude tosylate (15.3 g) in THF (135 mL) was added to a solution of sodium telluride (containing polytellurides) at 50-55 °C prepared by reduction of elemental Te (0.610 g, 4.78 mmol) with rongalite (21.9 g, 142 mmol) and aqueous NaOH (142 mL, 1 M) in an argon atmosphere. A smaller volume of THF may be used without difficulty. After 3 h, the reaction was complete as indicated by thin layer chromatography.[11] The reaction mixture was exposed to air and a stream of air was passed through it (0.5 h) to oxidize excess Te^{2-} to Te^0. The elemental tellurium is removed by filtration through Celite followed by washing the filter pad with ether. The ether and aqueous layers were separated and the latter was extracted with ether (2x25 mL). The combined ether extracts were dried ($MgSO_4$), and the ether was removed to give a yellow oil that was purified by distillation (Kugelrohr, 30-35 °C, 0.4 mm) to yield (+)-linalool as a colorless oil [6.75g, 43.8 mmol, 97% based on (2*S*, 3*S*)-epoxygeraniol corrected for the amount used to obtain a sample of purified epoxy tosylate.]: $[\alpha]_D^{22}$ +17.01° (neat, corrected for density) [lit[10] (-)-linalool $[\alpha]_D^{23}$ -17.04° (neat)].

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6. All compounds in the tables have been reported previously (see Ref. 1).

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8. This seems to be the case in reactions of glycidyl acetates which undergo deoxygenation and deacetylation only when a Lewis-acid forming reducing agent ($NaBH_4$, $LiEt_3BH$) is present: Dittmer, D.C.; Zhang, Y.; Discordia, R.P. *J. Org. Chem.* **1994**, *59*, 1004-1010.

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11. The product linalool and precursor, epoxygeranyl tosylate, have nearly the same R_f but the latter is UV active during visualization whereas the former is not.

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