Tetrahedron Letters,Vol.27,No.46,pp 5579-5582,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

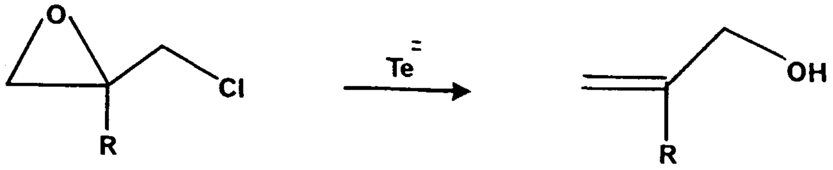
FUNCTIONAL GROUP MODIFICATION VIA ORGANOTELLURIUM CHEMISTRY. SYNTHESIS OF ALLYL ALCOHOLS FROM CHLOROMETHYLOXIRANES.

George Polson and Donald C. Dittmer*.
Department of Chemistry, Syracuse University
Syracuse, New York 13210

Summary: Treatment of 2-substituted-2-chloromethyloxiranes with telluride ion gives 2-substituted allyl alcohols, presumably through an epitelluride intermediate.

Recently organotellurium chemistry has caught the imagination of the organic chemist as a useful source of many synthetic transformations[1]. Although sulfide, selenide, and telluride ions are somewhat similar in their reactions with organic compounds[2], differences have been observed. For example, sulfides, selenides and tellurides are obtained with many organic halides, but allylic halides undergo coupling on treatment with telluride ions.[3] In studies of reactions of sulfide, selenide and telluride ions with chloromethyloxiranes, we have observed that whereas the sulfide dianion preferentially forms the four-membered thietanes,[4] selenide ion forms both the four-membered heterocycle[5] and a non-selenium containing allyl alcohol. Telluride ion, in contrast, forms only the allyl alcohol, without any trace of the four-membered ring (Equation 1).

(1)

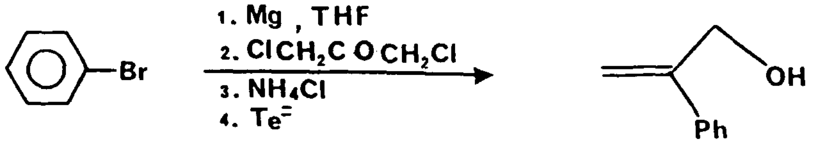


A survey of tellurium chemistry in recent years shows the effectiveness of telluride species in chemical transformations. Suzuki, Osuka, and Taka-Oka have reported regioselective reduction of α,β-epoxy ketones to β-hydroxy ketones using sodium hydrogen telluride[6] and Barton, Fekih and Lusinchi have reported formation of telluro-alcohols with regiospecificity corresponding to an S_N2 opening of an epoxide.[7]. These telluro-alcohols could be converted to olefins by use of p-toluenesulfonyl chloride. The mechanism of this transformation is suggested to involve an epitelluride which spontaneously loses elemental tellurium to give the corresponding olefin.

We have observed that treatment of the epoxide of trans-cinnamyl chloride with telluride ion produces on prolonged heating only one compound, trans-cinnamyl alcohol (entry 5 in Table I) in 41% yield with the unreacted epoxide being recovered. This reaction gives an indication of the stereochemical and regiochemical integrity of the attack of the nucleophile.

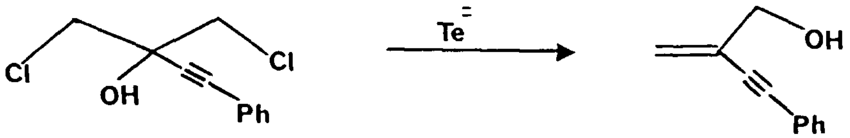
A "one-pot" synthesis of 2-phenyl-2-propene-1-ol can be effected starting with bromobenzene followed by successive treatment with magnesium, 1,3-dichloro-2-propanone, aqueous ammonium chloride and telluride ion. (Equation 2)

(2)



An abbreviated synthesis of 2-methylene-4-phenyl-3-butyn-1-ol involves addition of telluride ion in aqueous sodium hydroxide to the substituted dichloropropanol, it being reasoned that the oxirane would be formed in situ (Equation 3).

(3)



The formation of the allyl alcohols may involve an unstable epitelluride as shown in Scheme I. Episelenides have been observed by NMR at low temperature, but selenium is lost on warming to give the alkene.[8]

Scheme I

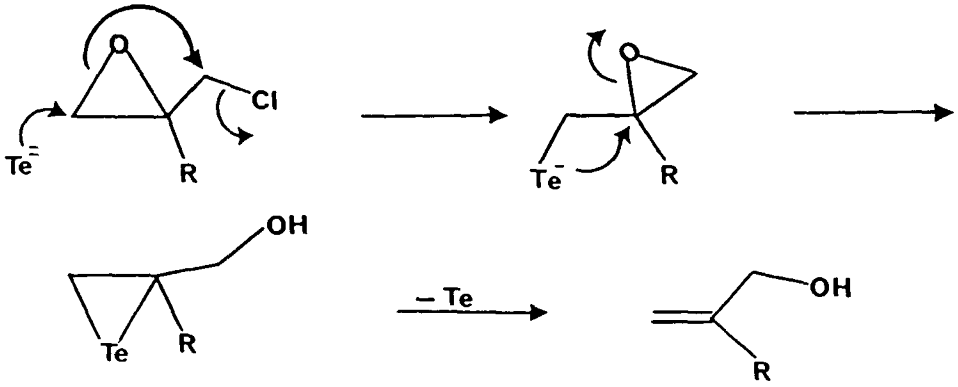
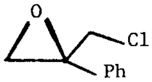
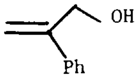
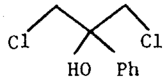
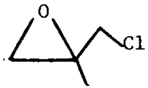
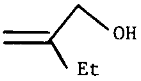
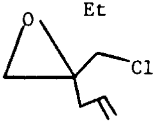
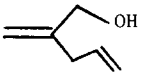
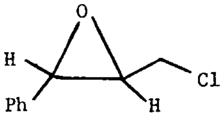
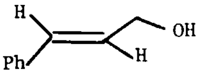
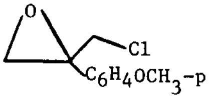
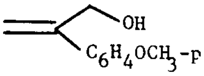
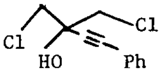


Table I lists the allyl alcohols prepared via the dihalopropanol. Yields have not been optimized. The overall reaction is equivalent to attachment of an alkyl or aryl substituent to the 2-position of 2-propen-1-ol.

TABLE I

Entry	Reactant[a]	Product[b]	Yield %[c]
1			90
2		—"—	85
3			40
4			43
5			41[d]
6			88
7			90

a) All the reactants except those of entry 5 were made by Grignard addition to 1,3-dichloro-2-propanone, followed by ring closure with a slurry of $Ca(OH)_2$ (modification of Ref. 9). The reactant of entry 5 was made from trans-cinnamyl chloride by mCPBA oxidation.

b) Products were fully characterized by IR, NMR, mass spectrometry and literature data.[10]

c) Isolated yields.

d) Reaction time 12 h; recovered epoxide (50%)

Our method provides an easy entry into the chemistry of relatively inaccessible allyl alcohols. Work is under way to optimize the yields and also to explore the scope of this reaction.

In a typical experiment 25 mL of aqueous sodium hydroxide solution was added to a flask containing 4.1 mmol of tellurium powder and 6.2 mmol of sodium hydroxymethanesulfinate, the reaction mixture being heated to 55°C for 0.5 h until all the tellurium was reduced yielding a purple telluride solution. To this was added 4.0 mmol of the 2-substituted chloromethyloxirane or the 2-substituted 1,3-dichloro-2-propanol in 20 mL of dioxane followed by refluxing for 4 h. The mixture was filtered through Celite (#545) and extracted with chloroform. The solvents were evaporated and the residue purified by flash chromatography or preparatory TLC on silica gel (ethyl ether: hexane, 3:7).

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

References and Notes

1. For recent reviews see a) Synthetic Applications of Tellurium Reagents. Petragnani N.; Comasseto J. V. Synthesis **1986**, 1. b) Synthetic Applications of Organotellurium Chemistry. Engman L. Acc. Chem Res. **1985**, 18, 274.
2. Brandsma L.; Wijers H. E. Recl. Trav. Chim. Pays-Bas **1963**, 82, 68.
3. Clive D. L. J.; Anderson P. C.; Moss N.; Singh A. J. Org. Chem. **1982**, 47, 1641.
4. a) Dittmer D. C.; Christy M. E. J. Org. Chem. **1961**, 26, 1324, b) B. Sjöberg, Svensk Kem. Tid. **1938**, 50, 250, c) Abbott, F.S.; Haya, K. Can. J. Chem. **1978**, 56, 71.
5. Dittmer D. C.; Polson G. Abstracts of Papers. 191st ACS National Meeting, Abstract #101, New York, N.Y., April, 1986.
6. Suzuki H.; Osuka A.; Taka-Oka K. Chem. Letters **1984**, 271.
7. Barton D. H. R.; Fekih A.; Lusinchi X. Tetrahedron Lett. **1985**, 26, 6197.
8. Chan T. H.; Finkenbine J. R. Tetrahedron Lett. **1974**, 2091.
9. Johnson F.; Panella J.P.; Carlson A. A. J. Org. Chem. **1962**, 27, 2241.
10. Products: Entry 1. Hatch, L.F.; Patton, T.L. J. Chem. Soc., **1954**, 2705; 3. Green, M.B.; Hickinbottom, W.J. J. Chem. Soc. Perkin I, **1957**, 3263; 4. Duboudin, J.G.; Jousseaume, B. J. Organometal. Chem. **1979**, 168, 1; 5, compared with authentic trans-cinnamyl alcohol (Aldrich); 6. m.p. 71-73°C; ^1H NMR ($CDCl_3$) δ 1.57 (br, s, OH), 3.82 (s, 3H, CH_3), 4.53 (s, 2H, CH_2), 5.26 (s, 1H, $=CH_2$), 5.40 (s, 1H, $=CH_2$), 6.87-6.91 (d, 2H), 7.39-7.43 (d, 2H); IR (KBr) 3600-3200 cm^{-1}, 1050 cm^{-1}; MS (70 eV) 164, 133, 121, 108, 77. 7. Salaün, J. J. Org. Chem., **1976**, 41, 1237.

(Received in USA 4 August 1986)