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# Alkenes from Cyclic Sulfates and Thionocarbonates of 1,2-Diols *via* Tellurium Chemistry

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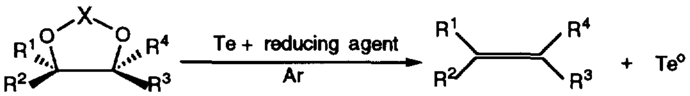
**Abstract:** Treatment of 1,2-diol cyclic sulfates (1,3,2-dioxathiolane 2,2-dioxides) with telluride ion, generated *in situ* by reduction of the element, yields alkenes rapidly (10 min- 2 h) under mild conditions (0 °C to room temperature). The reaction is stereospecific, e.g. *meso*-2,3-diphenylethane 2,3-diol → *cis*-stilbene; *d,l*-2,3-diphenylethane -2,3-diol → *trans*-stilbene. Unsaturated mannose and ribose derivatives have been obtained, and diethyl (-)-tartrate gives diethyl fumarate. The reaction may be performed with 0.1 equiv or less of elemental tellurium in the presence of a stoichiometric amount of reducing agent. Reaction of telluride ion with cyclic thionocarbonates (1,3-dioxolane-2-thiones) of *meso*- and *d,l*-1,2-diphenylethane-1,2-diol yields *cis*- and *trans*-stilbene, respectively.

1,2-Diols[1] are useful precursors of alkenes especially if mild and stereospecific procedures can be discovered that allow use in multistep syntheses of complex molecules.[2] One of the most notable previous methods is the stereospecific Corey-Winter reaction that involves treatment of cyclic thionocarbonates of 1,2-diols with a trivalent phosphorus reagent at elevated temperature (111 °C, trimethyl phosphite; 156 °C triethyl phosphite).[3a,b] Utilization of the more nucleophilic phosphine, 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine, permits lower temperatures (25-79 °C) to be employed (reaction times 2-24 h at 40 °C).[3c-g] Cyclic thionocarbonates also may be converted to alkenes by treatment with bis(1,5-cyclooctadiene)nickel [stereospecific, -78 °C → 25 °C, 1 h],[4a] iron pentacarbonyl[4b] [non-stereospecific, 140 °C, 2 h], Raney nickel,[4c] tri-*n*-butylstannane,[4d] or with Zn or Cr(II) and an alkyl iodide.[4e,f] The Eastwood process[5] involving 2-ethoxy-, 2-acyloxy-, and 2-dialkylamino-1,3-dioxolanes is limited by the requirement for electrophilic reagents and high temperature although 2-dialkylamino -1,3-dioxolanes yield alkenes at 20-50 °C on treatment with trifluoromethanesulfonic anhydride and diisopropylethylamine.[6] Base-induced fragmentation of 2-phenyl-1,3-dioxolanes suffers from the need to use a strong base (e.g. *n*-butyllithium) that restricts the kinds of functional groups that are allowed to be present. Somewhat less stereospecific methods, in addition to those already mentioned, are titanium and tungsten-mediated deoxygenations[7], the radical decomposition of vicinal dixanthates,[8] the nucleophilic reduction[9] and reductive elimination[10] of vicinal sulfonate esters, and the reductive elimination of cyclic phosphates,[11] phosphoroamidates,[11] and sulfates.[12]

We wish to report that cyclic sulfates[13a,b] of 1,2-diols give alkenes in high yields (Eq 1) on treatment with telluride ion generated *in situ* by reduction of elemental Te.[13c] Advantages include (1) the use of mild temperatures (0 °C to room temperature), (2) the rapidity of the reaction (10 min to 2 h), (3) stereospecificity, (4) the recovery of elemental Te formed in the nucleophilic reduction exemplified in Eq 1, and (5) the adaptability of the reaction to the use of 0.1 equiv or less of elemental Te.[13d] Cyclic sulfates of 1,2-diols are readily available *via* the "one-pot" method ($SOCl_2$, $NaIO_4$, $RuCl_3 \cdot 3H_2O$) of Sharpless and

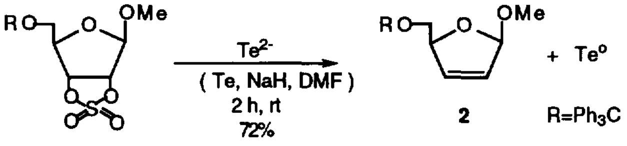
Gao.[13a] Previously, the conversion of cyclic sulfates to alkenes has been accomplished with low stereospecificity by sodium naphthalenide in THF:[12a] both (R*,S*) and racemic 1,2-diphenyl-1,2-ethanediol (*meso*- and *d,l*-hydrobenzoin, respectively) gave mixtures of (*E*)- and (*Z*)- stilbenes, the *E* isomer predominating. Application of this sodium naphthalenide method to the cyclic sulfate of diethyl (*L*)-(-)-tartrate did not give an alkene but instead, "a gross mixture".[12a] Our tellurium process gives 90% of (*Z*)-stilbene from the sulfate of *meso*-hydrobenzoin and 95% of (*E*)-stilbene from the sulfate of *d,l*-hydrobenzoin. The cyclic sulfate of diethyl (*L*)-(-)- tartrate gave diethyl fumarate (90%). The telluride ion used with this and other oxygenated functionalities should be prepared by reduction with sodium hydride in DMF[14] rather than with $LiEt_3BH$ in THF to avoid complications caused by the Lewis acid, $Et_3B$, presumably produced in the latter reduction.[15] When about 0.1 equiv of $Te^o$ is used with a stoichiometric amount of $LiEt_3BH$ in the reaction of **1a**, the borohydride and the cyclic sulfate are added alternately *via* addition funnels to the $Te^o$ suspension in THF, the color of the reaction mixture fluctuating between purple [excess $(Te_n)^{2-}$] and black (excess $Te^o$).



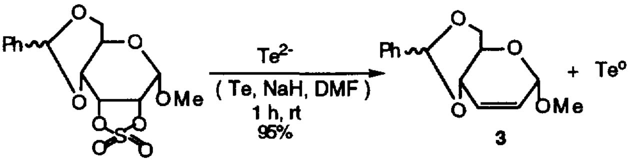
(1)[16,17]

| | X | R¹ | R² | R³ | R⁴ | Reducing agent | Solvent | °C | min | yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| **1 a** | $SO_2$ | Ph | H | Ph | H | $LiEt_3BH$ | THF | 0 | 20 | 95 |
| **b** | $SO_2$ | Ph | H | H | Ph | $LiEt_3BH$ | THF | 0 | 10 | 90 |
| **c** | $SO_2$ | $CO_2Et$ | H | $CO_2Et$ | H | NaH | DMF | 0 → rt | 30 | 90 |
| **d** | $SO_2$ | H | $-(CH_2)_8-$ | | H | $LiEt_3BH$ | THF | rt | 30 | 91 |
| **e** | CS | Ph | H | Ph | H | $LiEt_3BH$ | THF | rt | 5 | 71 |
| **f** | CS | Ph | H | H | Ph | $LiEt_3BH$ | THF | rt | 5 | 81 |

*Cis*-cyclic diol sulfates are readily converted to *cis*-alkenes exemplified by the reaction of **1d** and two unsaturated carbohydrate derivatives (Eq 2, 3)[18]. An attempt to convert *trans*-cyclooctanediol to *trans*-cyclooctene resulted only in formation of the *cis* isomer (57%). Formation of the unsaturated ribose derivative **2** in 72% yield (Eq 2) occurs in 2 h at room temperature in contrast to the synthesis of a similar derivative ( $R=PhCH_2$, 69% ) from the dimesylate and $Li_2Te$ at 105 °C for 20 h.[9c] A selenium-based process for the conversion of cyclic sulfates of 1,2-diols to unsaturated carbohydrate derivatives via a selenocyanate has been reported recently.[19] It involves an extra step, the conversion of the cyclic sulfate to a β-selenocyanatosulfate, the latter yielding the alkene on reduction with $NaBH_4$ in methanol.



(2)



(3)

The cyclic thionocarbonates, **1e** and **1f**, give good yields of *cis*- and *trans*- stilbene, respectively, but only a 13-29% yield of diethyl fumarate was obtained from the thionocarbonate of diethyl (-)-tartrate. Ethylene and propylene carbonates gave modest amounts of ethlene and propylene, respectively; but the cyclic carbonate of *meso*-hydrobenzoin ( **1b**, X=CO) gave the starting diol.

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16. $^{1}$H, $^{13}$C NMR spectra and mp (of solids) were identical with those of authentic samples.

17. *Typical experimental procedure*: Cyclic sulfate **1b** from *meso*-hydrobenzoin[13b], mp 70 °C (dec), (0.55 g, 2.0 mmol) in THF (3 mL) was treated with telluride ion obtained by reduction of Te (3.83 g, 3.0 mmol) with LiEt$_3$BH (6 mL, 1.0 M solution in THF), at 0 °C.[15a] Precipitation of Te was instantaneous and the reaction was complete in 2-10 min. Workup entailed passage of air through the well-stirred reaction mixture to oxidize unreacted Te$^{2-}$ ions. The black, elemental tellurium was removed by filtration through Celite, the filtrate was dried (MgSO$_4$), and concentration under reduced pressure gave *cis*-stilbene as an oil (0.33 g, 1.8 mmol, 90%) whose $^{13}$C and $^{1}$H NMR spectra were identical with those of authentic *cis*-stilbene. No trans isomer was detectable. To ensure removal of traces of any tellurium-containing product such as the putative epitelluride,[15a] a few drops of 3% hydrogen peroxide may be added.

18. The $^{1}$H NMR spectra are essentially identical with those reported for the known compounds: **2**, Leonard, N.J.; Sciavolino, F.C.; Nair, V. *J. Org. Chem.* **1968**, *63*, 3169-3174. **3**, Albano, E.; Horton, D.; Tsuchiya, T. *Carbohydrate Res.* **1966**, *2*, 349-362. The $^{13}$C NMR spectra of **2** and **3** also confirm their structures. The mp of **3** (118-120 °C) is comparable with that reported previously (119-120 °C).

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