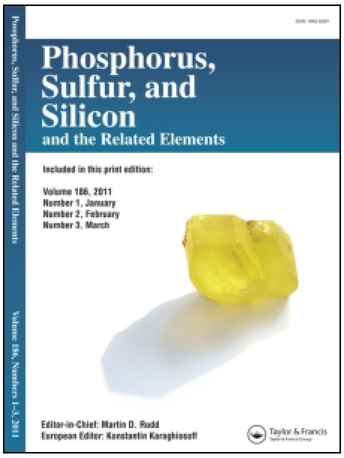

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FIRST ISOLATION AND STEREOCHEMISTRY OF OPTICALLY ACTIVE TELLUROXIDES

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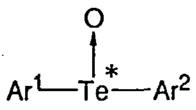
Optically active telluroxides **1** and **2** were isolated for the first time by means of medium-pressure liquid chromatography using an optically active column. Absolute configuration of the telluroxides (+)-**1** and (+)-**2** was determined to be *R* based on their specific rotations and circular dichroism spectra. The configurational lability and mechanism for racemization *via* an achiral hydrate were clarified by kinetic study and isotope tracer experiment.

Keywords: telluroxides; optical resolution; optically active column; stereochemistry; circular dichroism spectra; racemization

INTRODUCTION

There have been several reports on the isolation of optically active selenoxides.[1] However, optically active telluroxide has not yet been isolated, perhaps because telluroxides undergo racemization *via* an achiral hydrate much faster than selenoxides. We report here the isolation of optically active telluroxides, which are kinetically stabilized toward racemization by bulky substituents, by means of optical



1: Ar^1 = mesityl; Ar^2 = 2,4,6-tri-*t*-butylphenyl
2: Ar^1 = phenyl; Ar^2 = 2,4,6-tri-*t*-butylphenyl
3: Ar^1 = mesityl; Ar^2 = 2,4,6-triisopropylphenyl
4: Ar^1 = phenyl; Ar^2 = 2,4,6-triisopropylphenyl

resolution using an optically active column.[2] Their stereochemistry and configurational labilities are also examined.

RESULTS AND DISCUSSION

Asymmetric diaryl telluroxides **1**, **2**, **3**, and **4** were subjected to an optically active column, packed with amylose carbamate derivative / silica gel, using high-performance liquid chromatography at an analytical scale. Racemic telluroxides **1**, **2**, and **3** were resolved into two peaks corresponding to the enantiomers, as shown in Figure 1, while telluroxide **4** which has less bulky substituents showed only one peak. The chromatogram of telluroxide **3** showed an unusual shape which indicated that racemization was occurring in the column parallel to the resolution. These results show that a substituent more bulky than 2,4,6-triisopropylphenyl group is needed to inhibit racemization.

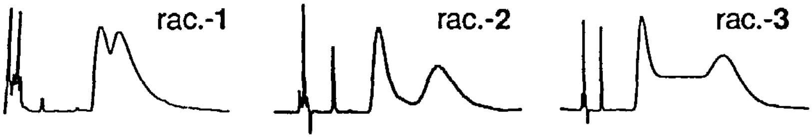


FIGURE 1 Chromatographic separation of racemic telluroxides **1**, **2**, and **3** on the optically active column by means of HPLC.

We attempted to resolve the racemic telluroxides **1** and **2** into their optical isomers at a preparative scale using medium-pressure liquid chromatography with the same type of column. In the optical resolution of telluroxide **2**, the first eluted enantiomer had a positive optical rotation {$[\alpha]_D$ +123.0 (*c* 0.16, MeCN)} and the second enantiomer had a negative optical rotation {$[\alpha]_D$ -68.8 (*c* 0.23, MeCN)}. However, the optical purities corresponding to the specific rotations could not be determined because racemization occurred readily. Optically pure telluroxide (+)-**1** {$[\alpha]_D$ +22.5 (*c* 0.36, MeCN)} was finally obtained (20 mg) from the faster eluent by repeated resolution (two times), and its optical purity was confirmed by ^{1}H-NMR measurement in the presence of dimethyl *L*-(+)-tartrate as an optically active shift reagent. At the same time, optically active telluroxide (-)-**1** {$[\alpha]_D$ -21.3 (*c* 0.38, MeCN)} was obtained in 93% optical purity from the later eluent.

Optically active telluroxides (+)-**1** and (+)-**2** show positive first Cotton effects at 313 and 305 nm (benzenoid transition), respectively, in their circular dichroism spectra (Figure 2), and (-)-**1** and (-)-**2** show negative first Cotton effects in the corresponding regions. These first Cotton effects show good correspondence with those of optically active selenium analogue, 2,4,6-tri-*t*-butylphenyl phenyl selenoxides (*R*)-(+)-**5** and (*S*)-(-)-**5**.[3] Thus, the absolute configuration of telluroxides (+)-**1** and (+)-**2** is assigned to be *R* and that of (-)-**1** and (-)-**2** is *S*.

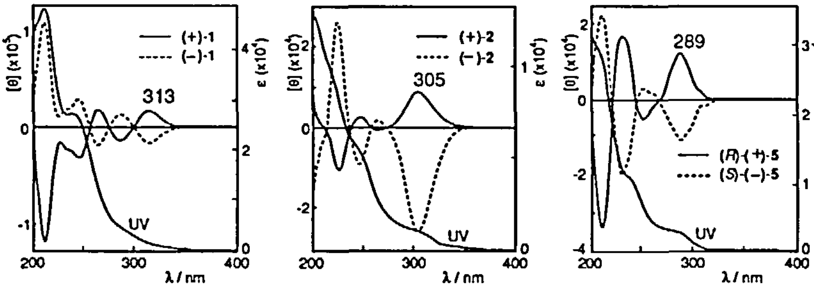
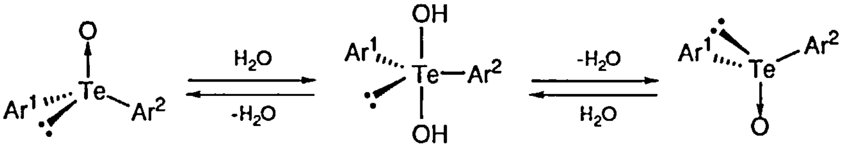


FIGURE 2 CD and UV spectra of optically active telluroxides **1** and **2** and selenoxides (*R*)-(+)-**5** and (*S*)-(-)-**5** in acetonitrile.

The stabilities of these telluroxides toward racemization were examined. In methanol that had been freshly distilled from Mg, racemization of telluroxide (+)-**1** (89% ee) was complete in about 1 day ($k = 6.05 \times 10^{-5}\ s^{-1}$; $t_{1/2} = 3.18$ h), whereas the specific rotation of (-)-**2** was completely lost within 5 minutes. A similar difference in the rate of racemization was observed in toluene that had been freshly distilled from CaH_2; i.e. the rate constants for racemization of (-)-**1** and (-)-**2** in toluene were $k = 3.08 \times 10^{-6}\ s^{-1}$ ($t_{1/2} = 62.5$ h) and $k = 9.71 \times 10^{-4}\ s^{-1}$ ($t_{1/2} = 0.20$ h), respectively. These results show that the combination of mesityl and 2,4,6-tri-*t*-butylphenyl groups as the substituents in a telluroxide is quite useful for inhibiting racemization. We previously reported that optically active selenoxide **5**, which has the same substituents as **2**, did not racemize in methanol even after 5 days.[4] Hence, optically active telluroxides are less stable toward racemization than optically active selenoxides.

The pyramidal inversion energies for dimethyl chalcogen oxides were estimated by *ab initio* MO calculations.[5] The pyramidal inversion energies for dimethyl-sulfoxide, selenoxide, and telluroxide were calculated to be 49.1, 53.2, and 63.9 kcal mol^{-1}, respectively. This result indicates the pyramidal inversion mechanism is not realistic for the racemization of telluroxides, at least at room temperature. Therefore, racemization may be catalyzed by a trace amount of water which remains in the solvent despite careful purification. Finally, the mechanism which involves the formation of an achiral tetracoordinate hydrate was confirmed by observation of the oxygen exchange reaction of telluroxide. When one drop of $H_2{}^{18}O$ (97 atom%) was added to a methanol solution of (+)-**1** (89% ee) and stirred at room temperature, the mass spectrum (Fab) showed 41% and 72% ^{18}O-enriched telluroxide at the points of 34% and 12% ee, respectively.



S-form Achiral Hydrate *R*-form

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[1.] For review, see: N. Kamigata and T. Shimizu, *Rev. Heteroatom Chem.*, 4, 226 (1991).
[2.] T. Shimizu, Y. Yamazaki, H. Taka, and N. Kamigata, *J. Am. Chem. Soc.*, **119**, 5966 (1997).
[3.] T. Shimizu and M. Kobayashi, *J. Org. Chem.*, **52**, 3399 (1987).
[4.] T. Shimizu, M. Kobayashi, and N. Kamigata, *Bull. Chem. Soc. Jpn.*, **61**, 3761 (1988).
[5.] All geometries were optimized using the second-order Møller-Presset perturbation (MP2) method. The double-zeta plus polarization basis set was used for hydrogen, carbon, oxygen, and sulfur atoms. The (5s4p2d/12s8p5d) and (10s8p4d/16s11p6d) basis sets were used for selenium and tellurium atoms, respectively.