# Isolation and Lability of Optically Active Telluronium Imides

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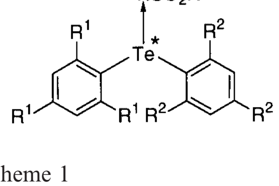
**Keywords:** Absolute configuration / Circular dichroism spectra / Optically active compounds / Racemization / Telluronium imides

Optically active telluronium imides have been isolated for the first time, by optical resolution of their racemic samples on an optically active column by medium-pressure column chromatography. The relationship between absolute configuration and their optical properties was clarified, and the mechanism for their racemization was also studied.

Many optically active tricoordinate sulfur compounds have been synthesized and are used as chiral sources in asymmetric synthesis.[1] Recently, some optically active tricoordinate selenium and tellurium compounds have also been isolated, and their properties and uses for asymmetric synthesis have been studied.[2−5] Optically active selenonium[6] and telluronium imides[7] are also used in asymmetric synthesis as important transient intermediates. We have recently reported the isolation of optically active selenonium imides, and their stereochemistry and configurational behavior have been clarified.[8,9] Telluronium imides, on the other hand, are believed to be much more unstable than the corresponding sulfonium and selenonium imides, even in racemic form, and few compounds have been synthesized.[10] Therefore, optically active telluronium imides have not yet been isolated. An electron-withdrawing group on the nitrogen atom is known to stabilize telluronium imides.[10] We have successfully synthesized some telluronium imides, stabilized not only thermodynamically with an electron-withdrawing group on the nitrogen atom, but also kinetically with bulky substituents, and have attempted to resolve them into their optical isomers (Scheme 1). We describe here the first isolation of enantiomerically pure telluronium imides by optical resolution, their stereochemistry, and their configurational lability.



**1**: R$^1$ = Me; R$^2$ = *i*Pr; R$^3$ = tolyl
**2**: R$^1$ = Et; R$^2$ = *i*Pr; R$^3$ = tolyl
**3**: R$^1$ = Et; R$^2$ = *i*Pr; R$^3$ = CF$_3$
**4**: R$^1$ = H; R$^2$ = *t*Bu; R$^3$ = CF$_3$

Scheme 1

The telluronium imide **1**, prepared from the corresponding telluroxide and toluene-4-sulfonamide, was loaded onto an optically active column packed with cellulose carbamate derivative/silica gel and subjected to high-performance liquid chromatography on an analytical scale with hexane/2-propanol (95:5) as the mobile phase. However, no peak corresponding to the imide was detected, while a peak attributable to the corresponding telluroxide was observed. With 2-propanol as the mobile phase, toluene-4-sulfonamide was also detected. These results indicated that hydrolysis of telluronium imide **1** had taken place on the column. In the case of telluronium imide **2**, with a bulkier substituent, two peaks corresponding to the two enantiomers of **2** were observed, as shown in Figure 1. This result clearly shows that a change in the bulkiness of the alkyl substituents on one of the benzene rings, from methyl to ethyl groups, had been very effective for stabilizing the telluronium imides to lead to hydrolysis. Similarly, telluronium imides **3** and **4** could also be optically resolved into their respective enantiomers.

The optical resolution of telluronium imides **2**, **3**, and **4** was carried out on the same type of chiral column on a preparative scale.[11] As a result, optically pure telluronium imides (+)-**2** {$[\alpha]^{25}_{D} = +55.0$ ($c$ = 0.44, MeCN)}, (+)-**3** {$[\alpha]^{25}_{D} = +79.0$ ($c$ = 0.52, MeCN)}, and (+)-**4** {$[\alpha]^{25}_{D} = +57.6$ ($c$ = 0.085, MeCN)} were obtained from the first-eluted fractions, respectively, and their optical purities were confirmed by HPLC analysis. Optically active (−)-isomers (−)-**2** {$[\alpha]^{25}_{D} = -53.2$ ($c$ = 0.65, MeCN)}, (−)-**3** {$[\alpha]^{25}_{D} = -82.3$ ($c$ = 0.20, MeCN)}, and (−)-**4** {$[\alpha]^{25}_{D} = -61.0$ ($c$ = 0.050, MeCN)} were also obtained in optically pure form from the second-eluted portions after repeated chromatographic separation.

The circular dichroism spectra of optically active telluronium imides (+)-**2**, (+)-**3**, and (+)-**4** showed positive first Cotton effects in acetonitrile at 285, 286, and 293 nm, respectively, while (−)-**2**, (−)-**3**, and (−)-**4** showed negative first Cotton effects in the corresponding regions, as shown

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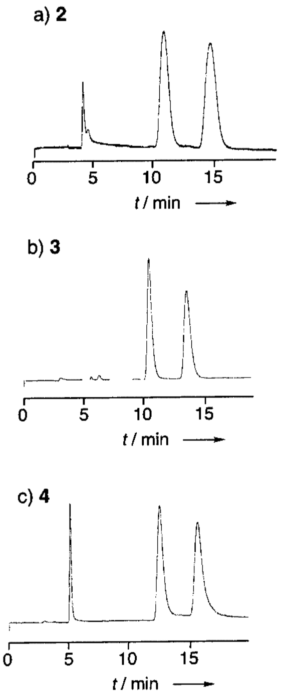


Figure 1. Chromatographic resolution of racemic telluronium imides **2−4** on an optically active column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD; 4.6 × 250 mm) by HPLC on an analytical scale at 25 °C. a) hexane/2-propanol (90:10); b) hexane/2-propanol (98:2); c) hexane/2-propanol (97:3).

in Figure 2. These first Cotton effects showed good correspondence with those of the optically active selenium analogue; (*R*)-(+)-*N*-[(phenyl)(2,4,6-tri-*tert*-butylphenyl)-selenonium] 4′-toluenesulfonimide showed a positive first Cotton effect at 272 nm, and the *S*-(−)-isomer a negative first Cotton effect, of which absolute configuration has been firmly established by X-ray crystallographic analysis of the (−)-isomer.[9] By comparison of their optical properties, the absolute configurations of telluronium imides (+)-**2**, (+)-**3**, and (+)-**4** were assigned as *R* and those of (−)-**2**, (−)-**3**, and (−)-**4** as *S*.

The optically active telluronium imide **2** was stable in the solid state under nitrogen, but racemization was observed in solution. The decrease in the optical purity of (*R*)-(+)-**2** in freshly distilled (from $CaH_2$) chloroform at 25 °C displayed a good linear relationship with first order rate plots ($k = 6.67 \times 10^{-6}\ s^{-1}$; $t_{1/2} = 28.9$ h). Racemization was also observed in carefully dried acetonitrile at 25 °C ($k = 5.00 \times 10^{-6}\ s^{-1}$; $t_{1/2} = 38.5$ h). One possible mechanism for racemization could be pyramidal inversion. However, the pyramidal inversion energies of telluronium imides have been calculated to be higher than those of the corresponding sulfur and selenium analogues; the pyramidal inversion energies for model molecules, *N*-(dimethylchalcogenonium) trifluoromethanimide, are 34.4 (chalcogen = S), 44.3 (chalcogen = Se), and 54.4 (chalcogen = Te) kcal mol$^{-1}$, respectively.[12] Racemization through the pyramidal inversion process therefore seemed unlikely, at least at room temperature. Edge inversion would also be a possible mechanism for racemization,[13] but this is improbable as the structure of the transition state is disfavored due to the bulky substituents.

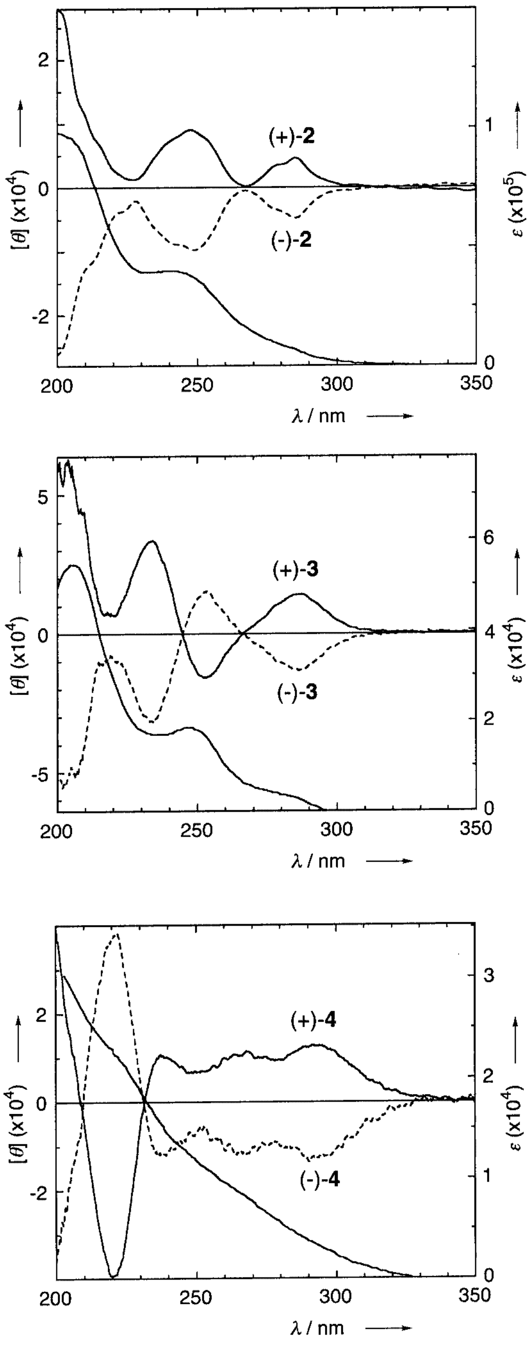
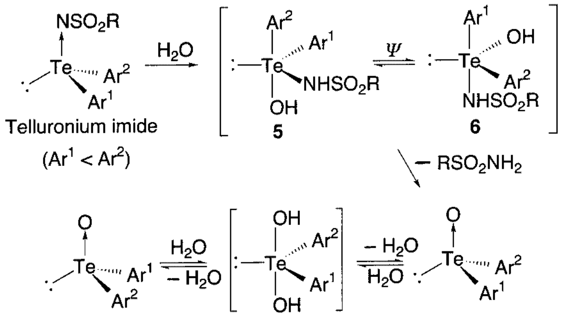


Figure 2. Circular dichroism spectra of optically active telluronium imides **2−4** in acetonitrile, with UV spectra of their racemic samples.

On the other hand, telluronium imides are easily hydrolyzed to give the corresponding telluroxides and amines.[10] It has previously been confirmed that optically active telluroxides readily racemize in the presence of a trace amount of water remaining in the solvent despite careful purification.[14,15] Therefore, the mechanism through the corresponding telluroxides, formed in situ by hydrolysis of the telluronium imides, would be the most plausible for the racemization of telluronium imides.

When a $CDCl_3$ solution of racemic telluronium imide **2** and phenyl 2,4,6-triisopropylphenyl telluroxide was stirred at room temperature, both *N*-[(phenyl)(2,4,6-triisopropylphenyl)telluronium] 4′-toluenesulfonimide and 2,4,6-triethylphenyl 2,4,6-triisopropylphenyl telluroxide were found together with the starting materials. This result indicates that telluronium imides and telluroxides exist in equilibrium, through hydrolysis of the imides and imination of the oxides. In basic solution, when (*R*)-(+)-**4** was stored in acetonitrile containing a large excess (65 equiv.) of sodium hydroxide, a Cotton effect for optically active telluroxide appeared, with a concomitant decrease in that of (*R*)-(+)-**4**, while no Cotton effect for the telluroxide was observed under neutral conditions, perhaps because of hydrolysis of the imide being slower than racemization of the telluroxide. Under acidic conditions, decomposition of the telluronium imide was observed. Since the stereochemistry of the resulting telluroxide formed under basic conditions was *R*,[14,15] the hydrolysis of telluronium imides had proceeded with retention of stereochemistry, at least under basic conditions. This result is different from that found with sulfonium imides. Sulfonium imides are known to be hydrolyzed with inversion of stereochemistry under basic conditions.[16] This difference in the mechanism of hydrolysis may be due to the ease of the formation of hypervalent tellurane as an intermediate, compared with that of sulfurane.

A plausible mechanism for our finding is as follows. The addition of water to the optically active telluronium imide from the side opposite the bulkiest substituent ($Ar^2$) gives tellurane **5** when catalyzed by $OH^-$ under basic conditions (Scheme 2). Telluranes **5** and **6** exist in equilibrium. Elimination of amide from the tellurane yields telluroxide with retention of stereochemistry, which then racemizes by addition and elimination of water.[14,15] Imination of the resulting racemized telluroxide gives the racemic telluronium imide.



Scheme 2

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[11] Typical procedure for optical resolution of telluronium imides: racemic telluronium imide (20 mg) in eluent (0.3 mL) was applied to an optically active column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD; 10 × 250 mm) and eluted with hexane containing 10 (for **2**), 2 (for **3**), and 3 (for **4**) vol% 2-propanol at flow rates of 1.5 for **2** and 1.0 mL $min^{-1}$ for **3** and **4**. About 6 mg of each optically active telluronium imide was collected from the first and the second eluates. In the case of **2**, optically pure (+)- and (−)-telluronium imides were obtained by the above procedure. With **3** and **4**, each eluate was again subjected to chromatographic resolution to give the optically pure telluronium imide. Their optical purities were determined by analytical scale HPLC analysis on the same type of chiral column (4.6 × 250 mm).

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