

Optically Active Telluronium Imides: Optical Resolution, Absolute Configuration, and Mechanism of Racemization

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ABSTRACT: *Thermodynamically and kinetically stabilized asymmetric diaryltelluronium imides were synthesized and optically resolved into their enantiomers on an optically active column using medium-pressure column chromatography. The relationship between the absolute configuration and the optical properties of the chiral telluronium imides was clarified. The mechanism of the racemization, which involves the formation of telluroxides by the hydrolysis of the telluronium imides, was proposed.* © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:523–529, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10185

INTRODUCTION

Many chiral tricoordinate sulfur compounds are known and used as chiral sources in asymmetric synthesis [1]. Some optically active tricoordinate selenium and tellurium compounds have also been isolated, and their properties and applicability to asymmetric reactions have been studied [2–5]. Optically active selenonium [6] and telluronium imides [7] have also been applied to asymmetric synthesis as important transient intermediates, and the

synthetic course via telluronium imides has been reported to show higher optical yields than that via the corresponding selenonium imides. However, to our knowledge, there had been no report concerning the isolation of optically active selenonium and telluronium imides, probably because selenonium and telluronium imides are unstable toward hydrolysis. Recently, we reported the isolation of optically active selenonium imides and clarified their stereochemistry and configurational stabilities [8,9]. On the other hand, telluronium imides are considered to be much more unstable toward hydrolysis [10] than the corresponding selenonium imides, and few compounds have been synthesized even in their racemic form [10,11]. Therefore, optically active telluronium imides have not yet been isolated so far. An electron-withdrawing group on the nitrogen atom is known to stabilize telluronium imides [11]. We successfully synthesized telluronium imides that were stabilized not only thermodynamically with an electron-withdrawing group on the nitrogen atom but also kinetically with bulky substituents on the tellurium atom, and attempted to resolve them into their optical isomers. We report herein the optical resolution of asymmetric telluronium imides, the absolute configuration, and mechanism of their racemization [12].

RESULTS AND DISCUSSION

Preparation of Racemic Telluronium Imides

Mesityl 2,4,6-triisopropylphenyltelluronium *N*-toluene-4'-sulfonimide (**1**) was synthesized by

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reacting the corresponding telluroxide, which was prepared by oxidation of telluride with *tert*-butyl hypochlorite [13], with toluene-4-sulfonamide in the presence of molecular sieves in 97% yield, as shown in Scheme 1. Similarly, bulkier telluronium *N*-toluene-4-sulfonimide **2** was obtained in 89% yield. However, a less bulky telluronium imide, phenyl 2,4,6-triisopropylphenyltelluronium *N*-toluene-4'-sulfonimide, could not be isolated because of facile hydrolysis although its formation was confirmed by ^1H NMR measurement of the reaction mixture. Telluronium *N*-trifluoromethanesulfonimide **3** was synthesized by reacting the corresponding telluroxide with trifluoromethanesulfonamide in the presence of sodium sulfate in 86% yield. In a similar reaction, telluronium *N*-trifluoromethanesulfonimide possessing a 2,4,6-tri-*tert*-butylphenyl group **4** could be obtained in 92% yield, whereas phenyl 2,4,6-tri-*tert*-butylphenyltelluronium *N*-toluene-4'-sulfonimide could not be synthesized because the reaction failed to proceed due to steric hindrance.

Optical Resolution of Telluronium Imides

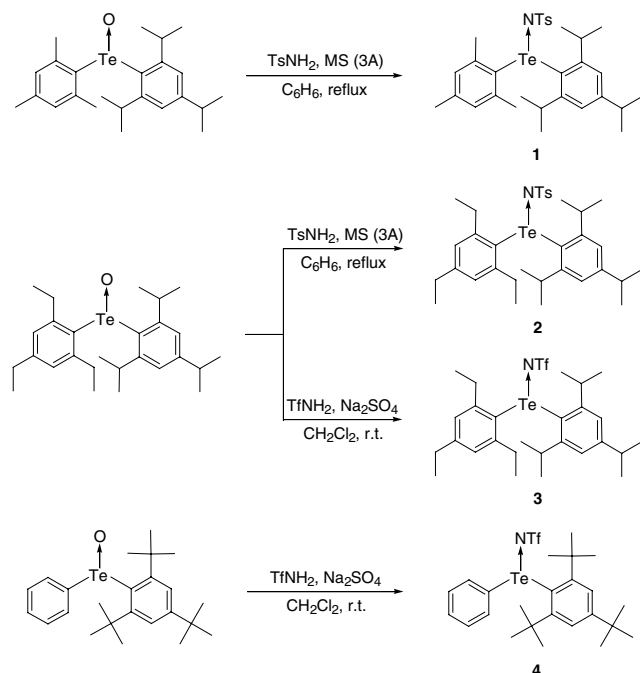
Telluronium imide **1** was subjected to high-performance liquid chromatography (HPLC) on an analytical scale by using an optically active column packed with cellulose carbamate derivative/silica gel and hexane/2-propanol (95/5) as the mobile phase. However, no peak corresponding to the telluronium imide was detected, whereas a peak assigned to the

corresponding telluroxide was observed. When 2-propanol was used as the mobile phase, a peak corresponding to toluene-4-sulfonamide was also detected. These results indicate that **1** was hydrolyzed in the column despite careful purification of the solvents. In the case of telluronium imide with a bulkier substituent **2**, two peaks corresponding to each of the enantiomers of **2** were observed, as shown in Fig. 1. This result clearly indicates that changing the alkyl substituents on one of the benzene rings from methyl to ethyl group is very effective for stabilizing the telluronium imides toward the hydrolysis. Similarly, telluronium *N*-trifluoromethanesulfonimides **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 a preparative scale using the same type of chiral column. As a result, optically pure telluronium imides (+)-**2**, (+)-**3**, and (+)-**4** were obtained from the respective first fractions that were eluted, as shown in Table 1, and their optical purities were confirmed by HPLC. Optically active (–)-isomers (–)-**2**, (–)-**3**, and (–)-**4** were also obtained in the optically pure form from the second-eluted portions by repeated chromatographic separations.

Circular Dichroism Spectra and Absolute Configuration of Optically Active Telluronium Imides

The circular dichroism spectra of optically active telluronium imides (+)-**2**, (+)-**3**, and (+)-**4**



SCHEME 1

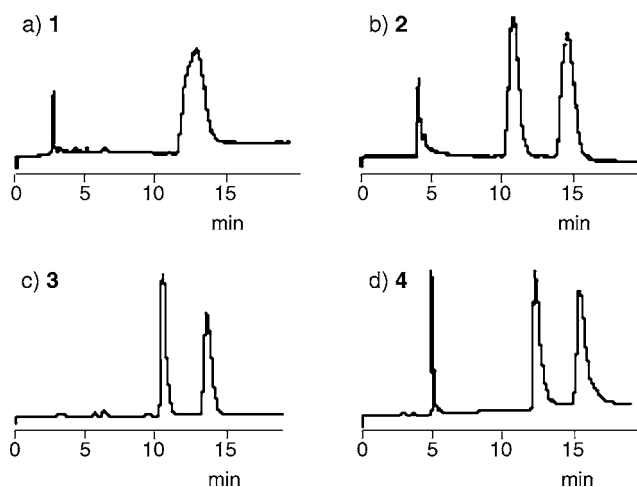


FIGURE 1 Optical resolution of telluronium imides **1–4** on an optically active column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD; 4.6×250 mm) by HPLC on an analytical scale at 25°C . (a) hexane/2-propanol (95/5); (b) hexane/2-propanol (90/10); (c) hexane/2-propanol (98/2); (d) hexane/2-propanol (97/3).

TABLE 1 Optical Resolution and Specific Rotation of Telluronium Imides 2–4^a

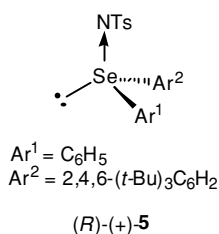
Compound	2-Propanol (%) ^b	First Enantiomer		Second Enantiomer	
		$[\alpha]_D$ (c) ^c	ee (%)	$[\alpha]_D$ (c) ^c	ee (%)
2	10	+55.0 (0.44)	100	–53.2 (0.65)	100
3	2	+79.0 (0.52)	100	–82.3 (0.20)	100
4	3	+57.6 (0.085)	100	–61.0 (0.050)	100

^aOptical resolution was carried out on an optically active column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD; 10 × 250 mm) by HPLC on a preparative scale at 25°C.

^bVolume percentage of 2-propanol in hexane used as mobile phase.

^cSpecific rotations were taken in acetonitrile at 25°C.

showed positive first Cotton effects in acetonitrile at 285, 286, and 293 nm, respectively, and (–)-2, (–)-3, and (–)-4 showed negative first Cotton effects in the corresponding regions, as depicted in Fig. 2. Those first Cotton effects showed good agreement with those of the optically active selenium analogue; the spectrum of (*R*)-(+)-phenyl 2,4,6-*tert*-butylphenylselenonium *N*-toluene-4'-sulfonimide (*R*)-(+)-5 showed a positive first Cotton effect at 272 nm, and that of the (*S*)-(–)-isomer showed a negative first Cotton effect, the absolute configuration of which has been clearly characterized by X-ray crystallographic analysis of the (–)-isomer [9]. Based on a comparison of the optical properties, the absolute configuration of telluronium imides (+)-2, (+)-3, and (+)-4 was assigned to the *R*-form and that of (–)-2, (–)-3, and (–)-4 to the *S*-form.



Configurational Stability and Mechanism of Racemization of Optically Active Telluronium Imides

Optically active telluronium imide (*R*)-(+)-2 was stable in the solid state under nitrogen; however, racemization was observed in solution. The decrease in the optical purity of (*R*)-(+)-2 showed a good linear relationship with the first-order rate plots in chloroform that had been freshly distilled from calcium hydride, at 25°C ($k = 6.67 \times 10^{-6} \text{ s}^{-1}$; $t_{1/2} = 28.9 \text{ h}$). Racemization was also observed in carefully dried acetonitrile at 25°C ($k = 5.00 \times 10^{-6} \text{ s}^{-1}$; $t_{1/2} = 38.5 \text{ h}$). Pyramidal inversion is one possible mechanism of the racemization. However, the barrier for the pyramidal inversion of telluronium imide has been calculated to be higher than those for the pyramidal inversion of the corresponding sulfur and selenium analogues; the pyramidal inversion energies for model molecules, dimethylchalcogen-onium *N*-trifluoromethanimides, are 34.4 (chalcogen = S), 44.3 (chalcogen = Se), and 54.4 (chalcogen = Te) kcal mol^{–1} [14]. Therefore, racemization via the pyramidal inversion process seems unlikely, at least at room temperature. Edge inversion is also a possible mechanism of the racemization [15]; however, this is improbable because the structure of the transition

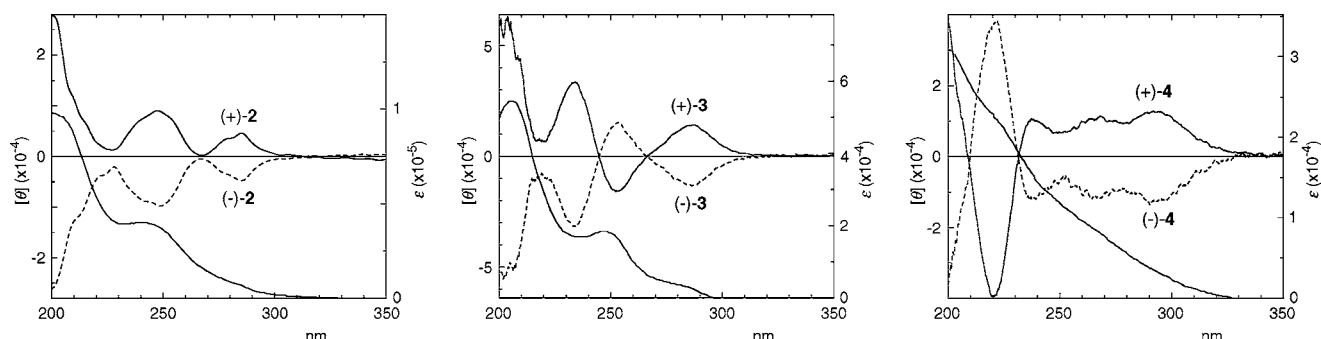
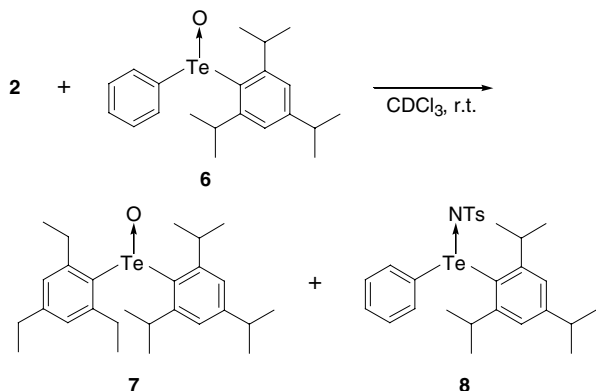


FIGURE 2 Circular dichroism spectra of optically active telluronium imides 2–4 in acetonitrile with UV spectra of their racemic samples.

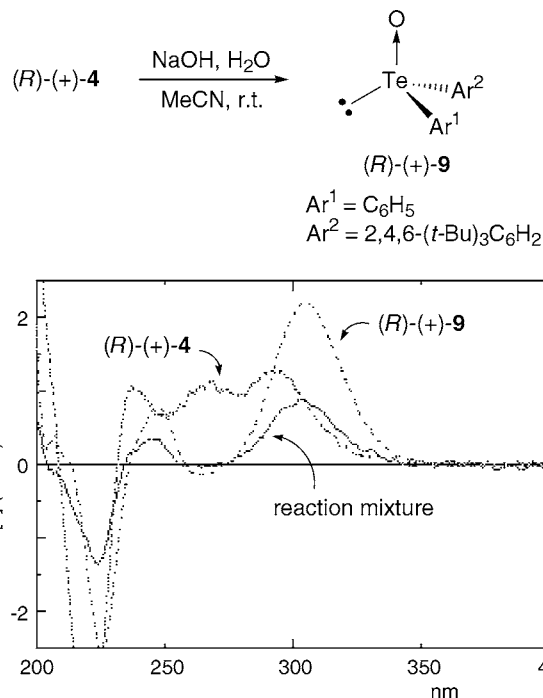
state is not favored because of the presence of bulky substituents.

On the other hand, telluronium imides are easily hydrolyzed to give the corresponding telluroxides and amines [11]. When a CDCl_3 solution of racemic telluronium imide **2** and phenyl 2,4,6-triisopropylphenyl telluroxide (**6**) was stored at room temperature, both 2,4,6-triethylphenyl 2',4',6'-triisopropylphenyl telluroxide (**7**) and phenyl 2,4,6-triisopropylphenyltelluronium *N*-toluene-4'-sulfonimide (**8**) were found together with the starting materials (Scheme 2). Furthermore, a CDCl_3 solution of phenyl 2,4,6-tri-*tert*-butylphenyl telluroxide and trifluoromethanesulfonamide yielded telluronium imide **4** together with the starting materials at room temperature even without sodium sulfate. These results indicate that telluronium imides and telluroxides exist in equilibrium through hydrolysis of the imides and imination of the oxides. We previously clarified that optically active telluroxides readily racemize in the presence of a trace amount of water remaining in the solvent despite careful purification [13,16]. Therefore, the mechanism involving the corresponding telluroxides, which are formed in situ by hydrolysis of the telluronium imides, is the most plausible for the racemization of telluronium imides.

When optically active telluronium imide (*R*)-(+)-**4** was stored in acetonitrile (3.3×10^{-5} M) containing a large excess (65 equiv) of 1 N NaOH solution, Cotton effects corresponding to optically active telluroxide (*R*)-(+)-**9** [13] appeared immediately with a decrease in that of (*R*)-(+)-**4** (Fig. 3), whereas no Cotton effect for the telluroxide was observed when (*R*)-(+)-**4** was hydrolyzed under neutral conditions, probably because racemization of the resulting telluroxide occurred more rapidly than hydrolysis of the imide under neutral conditions. Under acidic conditions, decomposition of the telluronium imide was observed.



SCHEME 2

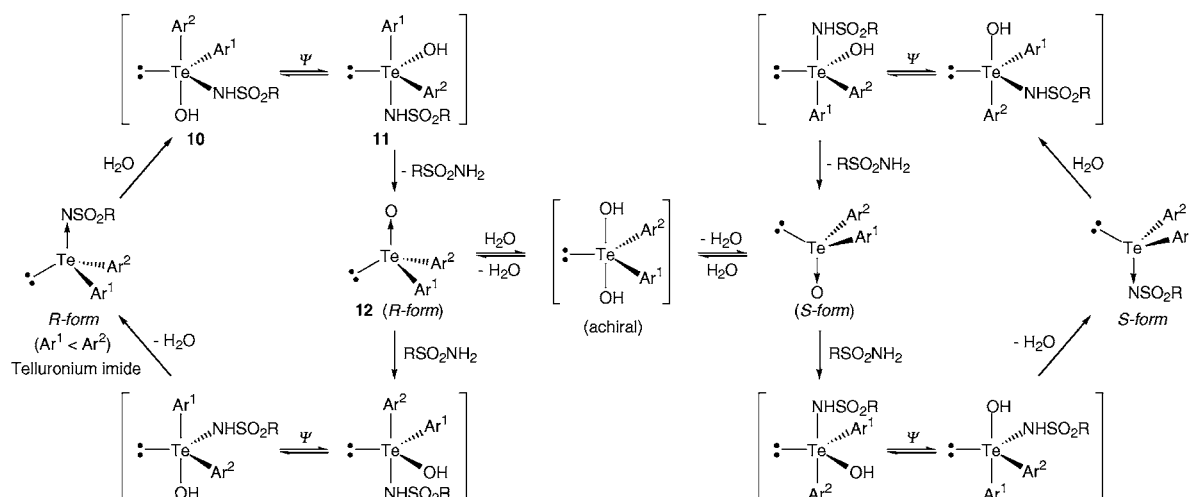
FIGURE 3 Hydrolysis of optically active telluronium imide (*R*)-(+)-**4** under basic conditions.

Since the stereochemistry of the resulting telluroxide formed under basic conditions was *R* [13,16], the hydrolysis of telluronium imides proceeds with a retention of stereochemistry, at least under basic conditions. This result differs from that with sulfonium imide: sulfonium imides are known to be hydrolyzed with an inversion of stereochemistry under basic conditions [17]. 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 the racemization of telluronium imides under basic conditions is shown in Scheme 3. The addition of water to the optically active telluronium imide from the side opposite the bulkiest substituent (Ar^2) gives tellurane **10** catalyzed by OH^- under basic conditions. Telluranes **10** and **11** exist in equilibrium. Elimination of amide from the tellurane yields telluroxide **12** with a retention of stereochemistry, which then racemizes via an achiral hydrate [13,16]. Imination of the resulting racemized telluroxide gives the racemic telluronium imide.

CONCLUSION

Kinetically and thermodynamically stabilized telluronium imides were synthesized by reacting the corresponding telluroxides with amides. Optically



SCHEME 3

active telluronium imides were isolated by chromatographic resolution on a chiral column. The relationship between the absolute configuration and the optical properties was clarified by comparison with that of optically active selenonium imides, which was previously determined by us. The mechanism of the racemization involving the formation of hyper-valent tellurane and telluroxide was also proposed.

EXPERIMENTAL

Hexane and benzene were distilled from sodium metal before use. Chloroform, dichloromethane, and 2-propanol were freshly distilled from calcium hydride. Acetonitrile was distilled from phosphorus(V) oxide before use. All reactions were carried out under nitrogen.

Preparation of Diaryl Telluroxides

Phenyl 2,4,6-triisopropylphenyl telluroxide [16], mesityl 2,4,6-triisopropylphenyl telluroxide [13], 2,4,6-triethylphenyl 2',4',6'-triisopropylphenyl telluroxide, and phenyl 2,4,6-tri-*tert*-butylphenyl telluroxide [13] were prepared from corresponding tellurides by oxidation with *tert*-butyl hypochlorite in 69, 81, 62, and 86% yields, respectively [13].

Synthesis of Diaryl Telluronium Toluene-4-sulfonimides (*rac*-**1** and **2**)

Typically, a benzene solution (100 ml) of telluroxide (3.0 mmol) and toluene-4-sulfonamide (3.0 mmol) was refluxed for 12 h equipped with a Dean-Stark condenser including molecular sieves 3A (5 g). The

solution was concentrated under reduced pressure to give telluronium imide (**1**: 97%; **2**: 89%). Further purification was not carried out to prevent the hydrolysis during the handling.

Mesityl 2,4,6-Triisopropylphenyltelluronium Toluene-4'-sulfonimide (rac-1). mp 156–157°C (colorless solid). ^1H NMR (500 MHz, CDCl_3) δ 0.94 (d, 6H, $J = 6.7$ Hz), 1.12 (d, 6H, $J = 6.7$ Hz), 1.23 (d, 6H, $J = 6.7$ Hz), 2.25 (s, 3H), 2.31 (s, 3H), 2.45 (s, 6H), 2.86 (sep, 1H, $J = 6.7$ Hz), 3.45 (sep, 2H, $J = 6.7$ Hz), 6.83 (s, 2H), 7.03 (s, 2H), 7.07 and 7.68 (ABq, 4H, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 20.8, 21.3, 22.4, 23.6, 23.7, 24.3, 24.6, 34.1, 34.9, 124.0, 125.7, 126.1, 127.7, 128.7, 131.1, 140.1, 141.5, 142.5, 143.9, 153.2, 153.5; ^{125}Te NMR (158 MHz, CDCl_3) δ 991.0; IR (KBr) ν_{max} 3000–2760, 1590, 1560, 1460, 1380, 1270, 1125, 1020, 940, 845, 810, 740, 675, 565, 550 cm^{-1} ; UV (MeCN) λ_{max} 209 (ϵ 4.6×10^4), 242 (ϵ 3.3×10^4), 286 (sh, ϵ 5.5×10^3) nm; MS m/z 621 (^{130}Te , M^+), 619 (^{128}Te , M^+), 452, 203, 119; HRMS calcd for $\text{C}_{31}\text{H}_{41}\text{NO}_2\text{S}^{130}\text{Te}$ 621.1925, found 621.1900.

2,4,6-Triethylphenyl 2',4',6'-Triisopropylphenyltelluronium Toluene-4'-sulfonimide (rac-2). Colorless viscous oil. ^1H NMR (500 MHz, CDCl_3) δ 0.96 (d, 6H, $J = 6.7$ Hz), 1.01 (t, 6H, $J = 7.6$ Hz), 1.09 (d, 6H, $J = 6.7$ Hz), 1.17 (t, 3H, $J = 7.6$ Hz), 1.21 (d, 6H, $J = 6.7$ Hz), 2.31 (s, 3H), 2.57 (q, 2H, $J = 7.6$ Hz), 2.75–2.97 (m, 5H), 3.49 (sep, 2H, $J = 6.7$ Hz), 6.92 (s, 2H), 7.02 (s, 2H), 7.07 and 7.69 (ABq, 4H, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 15.4, 15.7, 21.3, 23.7, 24.3, 24.6, 28.5, 28.7, 34.1, 34.7, 124.1, 125.8,

126.5, 128.3, 128.7, 128.8, 140.0, 144.0, 148.0, 148.7, 153.1, 153.3; ^{125}Te NMR (158 MHz, CDCl_3) δ 992.2; IR (neat) ν_{max} 3000–2700, 1590, 1560, 1460, 1260, 1125, 1080, 925, 670, 565, 550 cm^{-1} ; UV (MeCN) λ_{max} 242 (ϵ 4.0×10^4), 285 (sh, ϵ 7.8×10^3) nm; MS m/z 663 (^{130}Te , M^+), 661 (^{128}Te , M^+), 494, 203, 161; HRMS calcd for $\text{C}_{34}\text{H}_{47}\text{NO}_2\text{S}^{130}\text{Te}$ 663.2390, found 663.2362.

Synthesis of Diaryl Telluronium Trifluoromethanesulfonimides (rac-**3** and **4**)

Typically, a dichloromethane solution (20 ml) of telluroxide (1.0 mmol) and trifluoromethanesulfonamide (1.0 mmol) was stirred for desired period (**3**: 12 h; **4**: 1.5 h) in the presence of sodium sulfate (6 g) at room temperature. The solution was concentrated under reduced pressure to give telluronium imide (**3**: 86%; **4**: 92%). Further purification was not carried out to prevent the hydrolysis during the handling.

*2,4,6-Triethylphenyl 2',4',6'-Triisopropylphenyltelluronium Trifluoromethanesulfonimide (rac-**3**).* Colorless viscous oil. ^1H NMR (500 MHz, CDCl_3) δ 1.03 (d, 6H, $J = 6.6$ Hz), 1.10 (t, 6H, $J = 7.5$ Hz), 1.18–1.24 (m, 15H), 2.61 (q, 2H, $J = 7.5$ Hz), 2.75–3.01 (m, 5H), 3.44 (sep, 2H, $J = 6.6$ Hz), 6.99 (s, 2H), 7.09 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 15.2, 15.7, 23.6, 24.4, 28.4, 28.8, 34.1, 35.3, 119.3, 121.9, 124.6, 125.2, 128.9, 148.6, 148.7, 153.2, 153.9; ^{125}Te NMR (158 MHz, CDCl_3) δ 1028.6; IR (neat) ν_{max} 3000–2800, 1590, 1560, 1460, 1290, 1180, 1125, 1080, 988, 610, 570, 515 cm^{-1} ; UV (MeCN) λ_{max} 206 (ϵ 5.5×10^4), 249 (ϵ 1.9×10^4), 287 (sh, ϵ 3.7×10^3) nm; MS m/z 641 (^{130}Te , M^+), 639 (^{128}Te , M^+), 494, 203, 161. Anal. Calcd for $\text{C}_{28}\text{H}_{40}\text{F}_3\text{NO}_2\text{S}^{130}\text{Te}$: C, 52.61; H, 6.31; N, 2.19. Found: C, 52.61; H, 6.32; N, 2.10.

*Phenyl 2,4,6-Tri-tert-butylphenyltelluronium Trifluoromethanesulfonimide (rac-**4**).* mp 127–128°C (decomp, colorless prisms from dichloromethane); ^1H NMR (500 MHz, CDCl_3) δ 1.36 (s, 9H), 1.45 (s, 18H), 6.99–7.00 (m, 2H), 7.34–7.44 (m, 3H), 7.58 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 30.9, 33.6, 35.2, 39.3, 119.4, 122.0, 125.6, 126.2, 130.1, 131.7, 133.4, 154.6, 157.9; ^{125}Te NMR (158 MHz, CDCl_3) δ 1069.0; IR (KBr) ν_{max} 3000–2800, 1585, 1530, 1477, 1440, 1400, 1370, 1300, 1200, 1160, 1120, 975, 740, 690, 610, 570, 515 cm^{-1} ; UV (MeCN) λ_{max} 223 (sh, ϵ 2.2×10^4), 238 (sh, ϵ 1.6×10^4), 268 (sh, ϵ 8.3×10^3), 293 (sh, ϵ 3.8×10^3) nm; MS m/z 599 (^{130}Te , M^+), 597 (^{128}Te , M^+), 452, 245, 77; HRMS calcd for $\text{C}_{25}\text{H}_{34}\text{F}_3\text{NO}_2\text{S}^{130}\text{Te}$ 599.1325, found 599.1302.

Optical Resolution of Racemic Telluronium Imides by Means of Medium-Pressure Liquid Chromatography Using an Optically Active Column

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 a flow rate 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 second eluates, respectively. In the case of **2**, optically pure (+)- and (–)-telluronium imides were obtained by the above procedure. With **3** and **4**, each eluate was subjected to chromatographic resolution again to give the optically pure telluronium imide. Their optical purities were determined by HPLC analysis using the same type of chiral column (4.6×250 mm) at an analytical scale.

*Compound (R)-(+)-**2**.* Colorless viscous oil; 100% ee; $[\alpha]_D +55.0$ (c 0.44, MeCN); CD (MeCN) λ_{max} 248 ($[\theta] + 9.0 \times 10^3$), 285 ($[\theta] + 4.6 \times 10^3$) nm. ^1H and ^{13}C NMR spectra were almost same with those of racemic one.

*Compound (S)-(–)-**2**.* Colorless viscous oil; 100% ee; $[\alpha]_D -53.2$ (c 0.65, MeCN); CD (MeCN) λ_{max} 249 ($[\theta] - 9.8 \times 10^3$), 285 ($[\theta] - 4.8 \times 10^3$) nm. ^1H and ^{13}C NMR spectra were almost same with those of racemic one.

*Compound (R)-(+)-**3**.* Colorless viscous oil; 100% ee; $[\alpha]_D +79.0$ (c 0.52, MeCN); CD (MeCN) λ_{max} 208 ($[\theta] + 4.4 \times 10^4$), 218 ($[\theta] + 7.9 \times 10^3$), 234 ($[\theta] + 3.4 \times 10^4$), 252 ($[\theta] - 1.6 \times 10^4$), 286 ($[\theta] + 1.4 \times 10^4$) nm. ^1H and ^{13}C NMR spectra were almost same with those of racemic one.

*Compound (S)-(–)-**3**.* Colorless viscous oil; 100% ee; $[\alpha]_D -82.3$ (c 0.20, MeCN); CD (MeCN) λ_{max} 206 ($[\theta] - 5.2 \times 10^4$), 219 ($[\theta] - 8.2 \times 10^3$), 234 ($[\theta] - 3.2 \times 10^4$), 253 ($[\theta] + 1.5 \times 10^4$), 286 ($[\theta] - 1.3 \times 10^4$) nm. ^1H and ^{13}C NMR spectra were almost same with those of racemic one.

*Compound (R)-(+)-**4**.* Colorless viscous oil; 100% ee; $[\alpha]_D +57.6$ (c 0.085, MeCN); CD (MeCN) λ_{max} 220 ($[\theta] - 3.9 \times 10^4$), 237 ($[\theta] + 1.0 \times 10^4$), 247 ($[\theta] + 6.7 \times 10^3$), 268 ($[\theta] + 1.1 \times 10^4$), 278 ($[\theta] + 9.5 \times 10^3$), 293 ($[\theta] + 1.3 \times 10^4$) nm. ^1H and ^{13}C NMR spectra were almost same with those of racemic one.

Compound (S)-(-)-4. Colorless viscous oil; 100% ee; $[\alpha]_D -61.0$ (c 0.050, MeCN); CD (MeCN) $\lambda_{\max}$ 222 ($[\theta] + 3.8 \times 10^4$), 238 ($[\theta] - 1.2 \times 10^4$), 253 ($[\theta] - 5.7 \times 10^3$), 267 ($[\theta] - 1.1 \times 10^4$), 278 ($[\theta] - 9.0 \times 10^3$), 293 ($[\theta] - 1.3 \times 10^4$) nm. ^1H and ^{13}C NMR spectra were almost same with those of racemic one.

Kinetic Studies for Racemization of Optically Active Telluronium Imides

Kinetic studies on the racemization of optically active telluronium imide (*R*)-(+)-**2** were examined in chloroform and acetonitrile (ca. 7 mM) at 25°C. The rates of the racemization were calculated based on the specific rotation and plotted according to the first-order rate equation.

REFERENCES

- [1] (a) Metzner, P.; Thuillier, A. *Sulfur Reagents in Organic Synthesis*; Academic Press: London, 1993; (b) Patai, S.; Rappoport, A.; Stirling, C. J. M. (Eds.). *The Chemistry of Sulphones and Sulfoxides*; Wiley: New York, 1988; (c) Stirling, C. J. M.; Patai, S. (Eds.). *The Chemistry of the Sulphonium Group*; Wiley: New York, 1981; (d) Mikolajczyk, M.; Drabowicz, J. *Top Stereochem* 1982, 13, 333.
- [2] Shimizu, T.; Kamigata, N. *Org Prep Proced Int* 1997, 29, 603.
- [3] (a) Wirth, T. *Angew Chem, Int Ed Engl* 2000, 39, 3741; (b) Wirth, T. *Tetrahedron* 1999, 55, 1; (c) Nishibayashi, Y.; Uemura, S. *Rev Heteroatom Chem* 1996, 14, 83; (d) Komatsu, N.; Uemura, S. *Adv Detailed React Mechanisms* 1995, 4, 74.
- [4] (a) Back, T. G. (Ed.). *Organoselenium Chemistry*; Oxford University Press: New York, 1999; (b) Patai, S.; Rappoport, Z. (Eds.). *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1987; (c) Liotta, D. (Ed.). *Organoselenium Chemistry*; Wiley: New York, 1987; (d) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986.
- [5] (a) Shimizu, T.; Kamigata, N. *Rev Heteroatom Chem* 1998, 18, 11; (b) Kamigata, N.; Shimizu, T. *Rev Heteroatom Chem* 1991, 4, 226.
- [6] (a) Nishibayashi, Y.; Chiba, T.; Ohe, K.; Uemura, S. *J Chem Soc, Chem Commun* 1995, 1243; (b) Kurose, N.; Takahashi, T.; Koizumi, T. *J Org Chem* 1996, 61, 2932; (c) Takada, H.; Oda, M.; Miyake, Y.; Ohe, K.; Uemura, S. *J Chem Soc, Chem Commun* 1998, 1557; (d) Miyake, Y.; Oda, M.; Oyamada, A.; Takada, H.; Ohe, K.; Uemura, S. *J Organomet Chem* 2000, 611, 475.
- [7] Nishibayashi, Y.; Srivastava, S. K.; Ohe, K.; Uemura, S. *Tetrahedron Lett* 1995, 36, 6725.
- [8] (a) Shimizu, T.; Seki, N.; Taka, H.; Kamigata, N. *J Org Chem* 1996, 61, 6013; (b) Kamigata, N.; Taka, H.; Matsuhisa, A.; Matsuyama, H.; Shimizu, T. *J Chem Soc, Perkin Trans 1* 1994, 2257.
- [9] (a) Taka, H.; Shimizu, T.; Iwasaki, F.; Yasui, M.; Kamigata, N. *J Org Chem* 1999, 64, 7433; (b) Yasui, M.; Taka, H.; Shimizu, T.; Kamigata, N.; Iwasaki, F. *Acta Crystallogr C* 1999, 55, 1861.
- [10] Naddaka, V. I.; Gar'kin, V. P.; Sadekov, I. D.; Krasnov, V. P.; Minkin, V. I. *Zh Org Khim* 1979, 15, 896.
- [11] (a) Hellwinkel, D.; Fahrbach, G. *Justus Liebigs Ann Chem* 1968, 712, 1; (b) Otsubo, T.; Ogura, F.; Yamaguchi, H.; Higuchi, H.; Sakata, Y.; Misumi, S. *Chem Lett* 1981, 447; (c) Naddaka, V. I.; Avanesyan, K. V.; Cherkinskaya, M. L. *Zh Org Khim* 1989, 25, 367.
- [12] Preliminary communication: Shimizu, T.; Machida, Y.; Kamigata, N. *Eur J Org Chem* 2002, 2265.
- [13] Taka, H.; Yamazaki, Y.; Shimizu, T.; Kamigata, N. *J Org Chem* 2000, 65, 2127.
- [14] Shimizu, T.; Kamigata, N.; Ikuta, S. *J Chem Soc, Perkin Trans 2* 1999, 1469.
- [15] (a) Dixon, D. A.; Arduengo, A. J., III; Fukunaga, T. *J Am Chem Soc* 1986, 108, 2461; (b) Arduengo, A. J., III; Dixon, D. A.; Roe, D. C. *J Am Chem Soc* 1986, 108, 6821; (c) Dixon, D. A.; Arduengo, A. J., III; *J Am Chem Soc* 1987, 109, 338.
- [16] Shimizu, T.; Yamazaki, Y.; Taka, H.; Kamigata, N. *J Am Chem Soc* 1997, 119, 5966.
- [17] Cram, D. J.; Day, J.; Rayner, D. R.; von Schrititz, D. M.; Duchamp, D. J.; Garwood, D. C. *J Am Chem Soc* 1970, 92, 7369.