

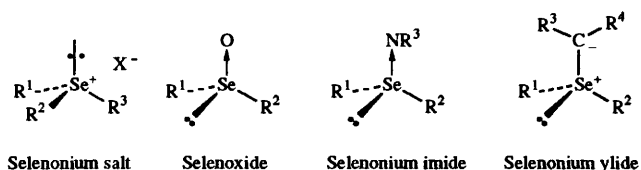
# Synthesis and stereochemistry of optically active telluronium ylides

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Diastereoisomeric mixtures of 1-{4-[(–)-menthyloxycarbonyl]phenyl(methyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-**5a, b** and 1-{4-[(–)-menthyloxycarbonyl]phenyl(2,4,6-triisopropylphenyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-**12a, b** have been synthesized. Optical resolution by the fractional recrystallization of dia.-**5a, b** and dia.-**12a, b** from hexane–dichloromethane gave the optically active (+)<sub>Te</sub>-telluronium ylides (+)<sub>Te</sub>-**5a** and (+)<sub>Te</sub>-**12a** as stable crystals, respectively. The absolute configuration of (+)<sub>Te</sub>-**5a** has been determined to be *R* based on the CD spectrum. The kinetics for the epimerization by pyramidal inversion of the optically active telluronium ylide (+)<sub>Te</sub>-**12a** have been studied.

A number of tricoordinate optically active sulfur compounds have already been synthesized, and their chemical and physical properties widely studied.<sup>1</sup> Recently our interest has been focused on the synthesis and stereochemistry of optically active tricoordinate selenium compounds. We have isolated and reported some optically active tricoordinate tetravalent selenium compounds such as selenonium salts,<sup>2</sup> selenoxides,<sup>3,4</sup> selenonium imides<sup>5</sup> and selenonium ylides,<sup>6,7</sup> and clarified their stereochemistry, reactivities and physical properties.



Tellurium is an elemental homologue of sulfur and selenium. However, little work has been reported on optically active tellurium compounds<sup>8</sup> in spite of the fact that many tellurium compounds are considered to have similar structures to the corresponding sulfur and selenium compounds. In the course of our investigations on optically active tricoordinate selenium compounds, our research interest turned to the synthesis of optically active tellurium compounds and also to the study of the stereochemistry and some chemical and physical behaviours. We have succeeded in synthesizing optically active telluronium ylides as stable crystals, clarified their stereochemistry, and studied the kinetics of epimerization by pyramidal inversion. The results are described herein.

## Results and discussion

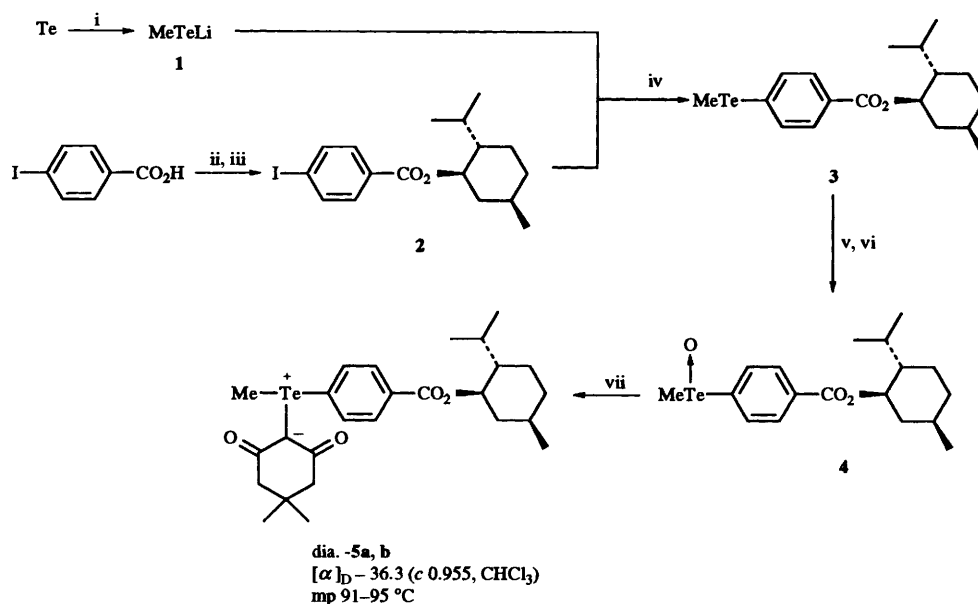
The first preparation of telluronium ylides was reported by Freeman and co-workers in 1970,<sup>9</sup> however, they were unstable. Some years later, several stable telluronium ylides were synthesized by two different research groups independently<sup>10,11</sup> but these compounds were achiral. We planned to synthesize some diastereoisomeric mixtures of telluronium ylides and to isolate them in optically pure form by optical resolution. We designed asymmetric telluronium ylides possessing a (–)-menthyl group as a chiral source for optical resolution and tried to resolve them into their optically active forms by fractional recrystallization.

### Synthesis of diastereoisomeric mixtures of telluronium ylides

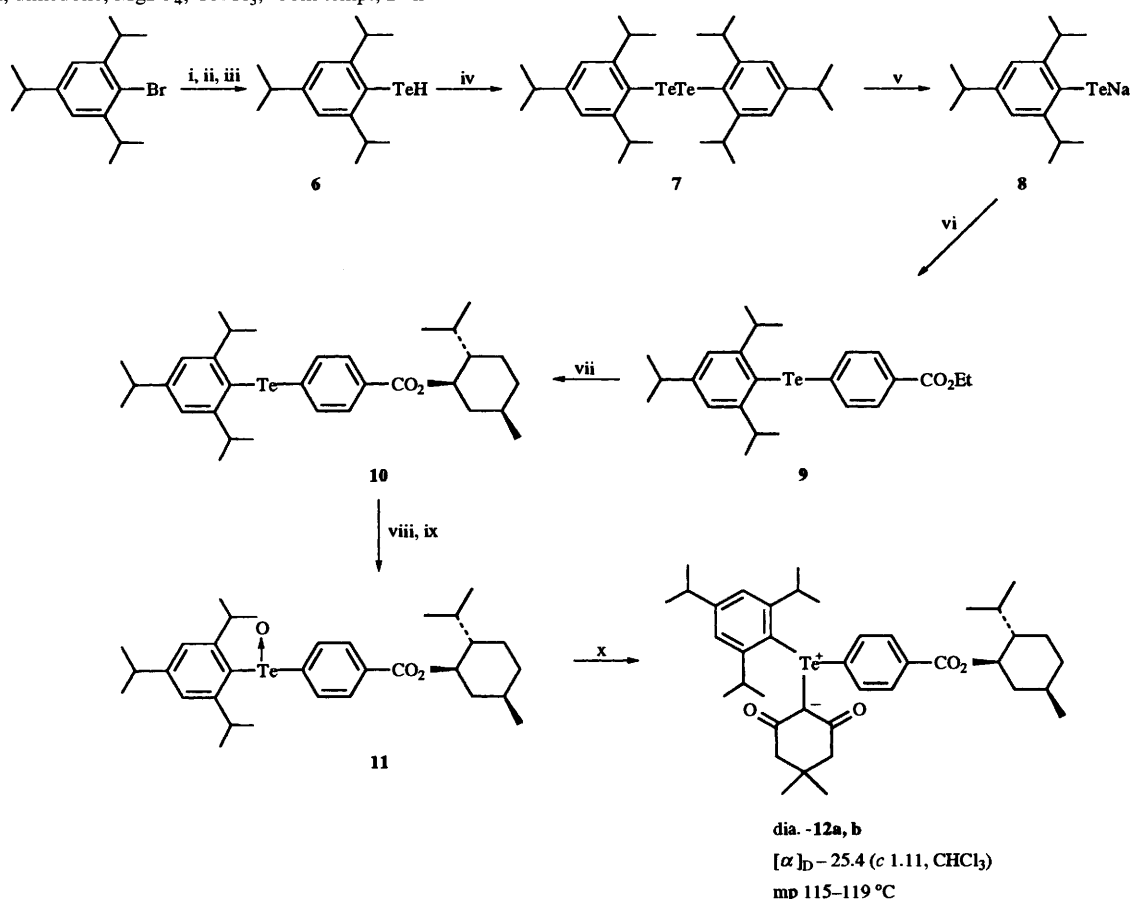
A diastereoisomeric mixture of 1-{4-[(–)-menthyloxycarbonyl]phenyl(methyl)telluroniumyl}-4,4-dimethyl-2,6-dioxo-

cyclohexan-1-ide dia.-**5a, b** was synthesized by the following procedures (Scheme 1). Reaction of lithium methanetelluroate **1**, prepared from methylithium and tellurium powder, with (–)-menthyl *p*-iodobenzoate **2** in THF gave 4-[(–)-menthyloxycarbonyl]phenyl methyl telluride **3** in 26% yield.<sup>12</sup> Oxidation of telluride **3** was achieved by treating it with *tert*-butyl hypochlorite in the presence of pyridine and methanol in dichloromethane at –25 °C gave a diastereoisomeric mixture of 4-[(–)-menthyloxycarbonyl]phenyl methyl telluroxide **4** in quantitative yield.<sup>13</sup> Reaction of telluroxide **4** with 5,5-dimethylcyclohexane-1,3-dione (dimedone) in the presence of anhydrous magnesium sulfate in chloroform afforded a diastereoisomeric mixture of 1-{4-[(–)-menthyloxycarbonyl]phenyl(methyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-**5a, b** in quantitative yield.<sup>11</sup> The [α]<sub>D</sub> value of the resulting ylide dia.-**5a, b** was –36.3 (*c* 0.955, CHCl<sub>3</sub>).

A diastereoisomeric mixture of 1-{4-[(–)-menthyloxycarbonyl]phenyl(2,4,6-triisopropylphenyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-**12a, b** was also synthesized by the following procedures (Scheme 2). Treatment of tellurium powder with 2,4,6-triisopropylphenyl magnesium bromide under reflux in THF followed by hydrolysis with dilute hydrochloric acid afforded 2,4,6-triisopropylbenzenetelluro<sup>14</sup> **6**. Compound **6** was oxidized by bubbling oxygen through an ethanol solution in the presence of a few pellets of sodium hydroxide to give bis(2,4,6-triisopropylphenyl) ditelluride **7** in 45% yield. Reaction of an ethanol solution of sodium 2,4,6-triisopropylbenzenetelluroate **8**, prepared by the reduction of ditelluride **7** with sodium borohydride, with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate<sup>15</sup> gave 4-(ethoxycarbonyl)phenyl 2,4,6-triisopropylphenyl telluride **9** in 32% yield. Transesterification of compound **9** was carried out using butyllithium and (–)-menthol to give 4-[(–)-menthyloxycarbonyl]phenyl 2,4,6-triisopropylphenyl telluride **10** in 92% yield.<sup>16</sup> Oxidation of telluride **10** with *tert*-butyl hypochlorite in the presence of pyridine and methanol gave a diastereoisomeric mixture of 4-[(–)-menthyloxycarbonyl]phenyl 2,4,6-triisopropylphenyl telluroxide **11** in quantitative yield.<sup>13</sup> Finally, a diastereoisomeric mixture of 1-{4-[(–)-menthyloxycarbonyl]phenyl(2,4,6-triisopropylphenyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-**12a, b** was obtained in quantitative yield by condensation of telluroxide **11** with dimedone in the presence of anhydrous magnesium sulfate.<sup>11</sup> The [α]<sub>D</sub> value of the ylide dia.-**12a, b** was –25.4 (*c* 1.11, CHCl<sub>3</sub>). Ylides dia.-**5a, b** and dia.-**12a, b** were stable in the crystalline state and in chloroform solution at room temperature.



**Scheme 1** Reagents and conditions: i, MeLi; ii,  $\text{SO}_2\text{Cl}_2$ ; iii, pyridine, (–)-menthol; iv, THF, 80 °C; v,  $\text{Bu}'\text{OCl}$ , pyridine, MeOH,  $\text{CH}_2\text{Cl}_2$ ; vi, aq. NaOH; vii, dimedone,  $\text{MgSO}_4$ ,  $\text{CHCl}_3$ , room temp., 24 h



**Scheme 2** Reagents and conditions: i, Mg, THF,  $\text{I}_2$ ; ii, Te; iii, dil. HCl; iv,  $\text{O}_2$ , NaOH, EtOH; v,  $\text{NaBH}_4$ , EtOH; vi,  $p\text{-EtO}_2\text{CC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$ , EtOH, 0 °C–room temp., 24 h; vii, BuLi, (–)-menthol, THF, 0 °C–room temp., 3 h; viii,  $\text{Bu}'\text{OCl}$ , pyridine, MeOH,  $\text{CH}_2\text{Cl}_2$ , –25 °C; ix, aq. NaOH; x, dimedone,  $\text{MgSO}_4$ ,  $\text{CHCl}_3$ , room temp., 24 h

### Optical resolution of telluronium ylides

A diastereoisomeric mixture of telluronium ylide dia.-5a, b  $\{[\alpha]_D - 36.3$  ( $c$  0.955,  $\text{CHCl}_3$ ) $\}$  was optically resolved by fractional recrystallization from hexane–dichloromethane. The absolute value of the specific rotation of the crystals obtained by the fractional recrystallization gradually decreased at every recrystallization, however, after five recrystallizations, it re-

mained constant. The optically active telluronium ylide, (+) $_{\text{Te}}$ -5a, thus obtained showed a specific rotation of  $[\alpha]_D - 7.9$  ( $c$  0.205,  $\text{CHCl}_3$ ). Similarly, optically active telluronium ylide, (+) $_{\text{Te}}$ -12a,  $\{[\alpha]_D - 8.8$  ( $c$  0.293,  $\text{CHCl}_3$ ) $\}$  was obtained as crystals after five recrystallizations from hexane–dichloromethane. The optical purities of (+) $_{\text{Te}}$ -5a and (+) $_{\text{Te}}$ -12a were estimated to be 30 and 25%, respectively, from  $^1\text{H}$  NMR

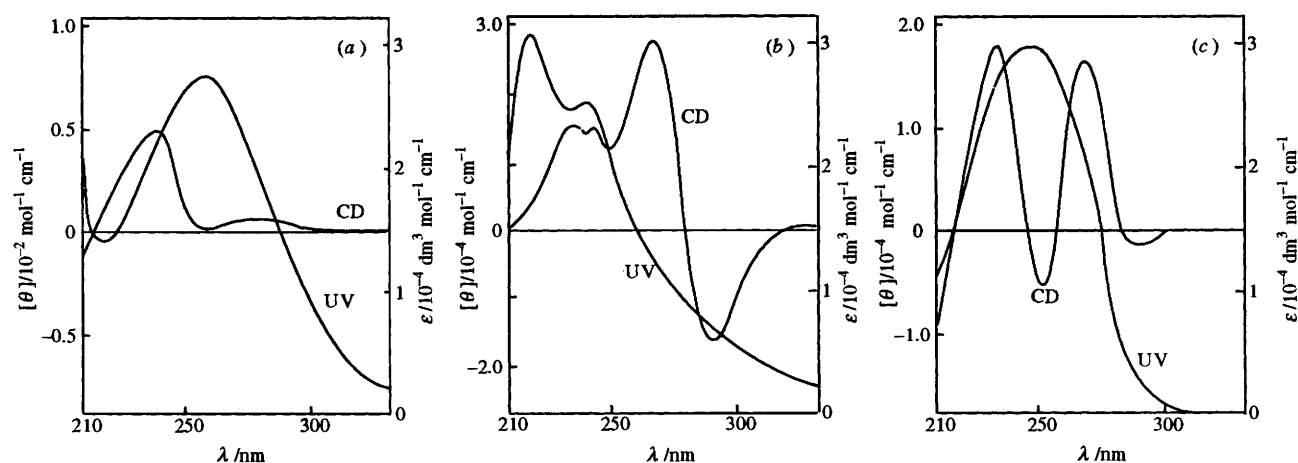


Fig. 1 The UV and CD spectra of optically active telluronium ylides (a) (+)- $T_{e}$ -5a, (b) (+)- $T_{e}$ -12a and (c) (R)-(+)- $S_{e}$ -13<sup>6</sup>

spectra (the methodology of which is described later). The optical purities of other diastereomeric isomers obtained from the corresponding mother liquor, (-)- $T_{e}$ -5b [ $\alpha$ ]<sub>D</sub> -38.3 (c 1.06, CHCl<sub>3</sub>) and (-)- $T_{e}$ -12b [ $\alpha$ ]<sub>D</sub> -32.3 (c 1.28, CHCl<sub>3</sub>), were very low (2% de in both compounds). The optical resolution of dia.-5a, b and dia.-12a, b was also attempted by HPLC using optically active columns. However, the telluronium ylides decomposed (or hydrolyzed) in silica gel columns such as Daicel Chiralpack AD or AS and Bakerbond chiral column. The ylides did not decompose but could not be resolved when Bakerbond cellulose-columns such as Chiralcel OB, OD, OF, OG, OJ and CA-1 columns were used.

We directed our efforts toward the isolation of one diastereoisomer of either (+)- $T_{e}$ -5a or (-)- $T_{e}$ -5b and (+)- $T_{e}$ -12a or (-)- $T_{e}$ -12b as the optically pure ylide from the corresponding diastereoisomeric mixtures, dia.-5a, b and dia.-12a, b, by optical resolution, unfortunately, we failed to isolate the optically pure form. We had expected to be able to achieve optical resolution from the diastereoisomeric mixture of telluronium ylides (dia.-5a, b and dia.-12a, b) since we have succeeded in isolating diastereomerically pure selenonium ylide possessing the same substituents around the selenium atom.<sup>6,7</sup> However, the present results are the first examples of the resolution of optically active telluronium ylides as stable crystals.

#### Determination of the optical purities of the telluronium ylides

The optical purities of the optically active telluronium ylides (+)- $T_{e}$ -5a, (-)- $T_{e}$ -5b, (+)- $T_{e}$ -12a and (-)- $T_{e}$ -12b were determined by <sup>1</sup>H NMR. The <sup>1</sup>H NMR signals of (+)- $T_{e}$ -5a and (-)- $T_{e}$ -5b are expected to be observed at different chemical shifts since they are diastereoisomers. However, no difference was observed between the spectra either in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> solution. The <sup>1</sup>H NMR spectrum of a diastereoisomeric mixture of telluronium ylides dia.-5a, b was then measured in the presence of a shift reagent, (*S*)-(-)-1,1'-bi-2-naphthol, in C<sub>6</sub>D<sub>6</sub> at 10 °C. The singlet proton signal for the methyl group bonded to the tellurium atom separated into two singlet signals. The signal strengths of the two singlet signals for the methyl groups were almost equal, showing that dia.-5a, b is a nearly 1:1 diastereoisomeric mixture. Thus, the optical purity of the telluronium ylide (+)- $T_{e}$ -5a obtained by the fractional recrystallization was calculated to be 30% de from the signal strength ratio of the methyl groups. Similarly, the optical purity of (-)- $T_{e}$ -5b was determined to be 2% de.

The <sup>1</sup>H NMR spectrum of the diastereoisomeric mixture of telluronium ylide dia.-12a, b was measured in C<sub>6</sub>D<sub>6</sub>. In this case, the singlet proton signal for methylene groups of the dimedone moiety was separated into two singlet signals without the addition of the shift reagent. Furthermore, the AB quartet

signal of the aromatic hydrogens of the [(-)-menthyloxy-carbonyl]phenyl moiety was also observed at different chemical shifts under the same conditions. The signal strengths of the two singlet signals of the methylene groups and the two AB quartet signals of the aromatic hydrogens were almost equal. Thus, the optical purities of (+)- $T_{e}$ -12a and (-)- $T_{e}$ -12b were determined to be 25 and 2% de, respectively, from their <sup>1</sup>H NMR signals of the methylene groups of dimedone moiety and aromatic hydrogens.

#### Determination of the absolute configuration of (+)- $T_{e}$ -5a

The CD spectra of optically active telluronium ylides (+)- $T_{e}$ -5a and (+)- $T_{e}$ -12a are shown in Fig. 1 together with that of optically pure selenonium ylide, (R)-(+)- $S_{e}$ -{4-[(*S*)-menthyloxy-carbonyl]phenyl(methyl)selenoniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide, (R)-(+)- $S_{e}$ -13, whose absolute configuration is determined to be *R* from the X-ray crystallographic analysis.<sup>6</sup> The CD spectra of (+)- $T_{e}$ -5a and optically pure selenonium ylide (R)-(+)- $S_{e}$ -13 show quite similar Cotton effects: *i.e.* the CD spectrum of (+)- $T_{e}$ -5a in methanol showed positive Cotton effects at 277 and 239 nm and that of optically pure selenonium ylide (R)-(+)- $S_{e}$ -13 showed positive Cotton effects at 266 and 234 nm in methanol. A slightly red shift was observed in the positive Cotton effects of (+)- $T_{e}$ -5a compared with that of the selenonium ylide 13; this observation is quite reasonable taking into consideration the difference between the asymmetric heteroatoms, tellurium and selenium. Thus, the absolute configuration of optically active telluronium ylide (+)- $T_{e}$ -5a is determined to be *R* since the substituents on the tellurium atom of (+)- $T_{e}$ -5a are the same as those on the selenium atom in optically pure selenonium ylide (R)-(+)- $S_{e}$ -13.

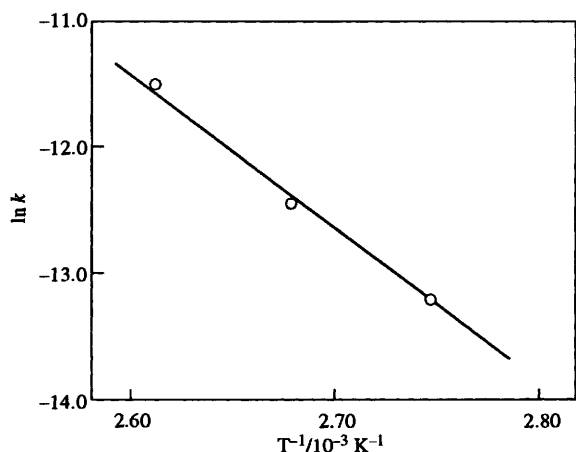
#### Stability of the telluronium ylides under various conditions

The stability of the telluronium ylides dia.-5a, b and dia.-12a, b towards acid, base, and water was examined. To a solution containing a diastereoisomeric mixture of telluronium ylide dia.-5a, b in chloroform was added one drop of conc. hydrochloric acid, and the solution was stirred for a while. The <sup>1</sup>H NMR spectrum showed that the ylide decomposed to unidentifiable complex compounds (*i.e.* the signal for the methyl proton bonded to the tellurium atom disappeared and the dimedone moiety dissociated). The ylide was also decomposed in some optically active silica gel columns such as DAICEL Chiralpack AD or AS using propan-2-ol-hexane (9:1) as the eluent. Then, to a solution containing a diastereoisomeric mixture of telluronium ylide dia.-5a, b in methylene chloride were added several drops of aqueous sodium hydroxide (1 mol dm<sup>-3</sup>), and the mixture was stirred at room temperature for 6 h; however, no difference was observed in the <sup>1</sup>H NMR spectrum. The

**Table 1** First order rate constants and activation parameters for the pyramidal inversion of (+)<sub>Tc</sub>-12a

Compound	Solvent	T/°C	k/10 <sup>-6</sup> s <sup>-1</sup>	E <sub>a</sub> kcal mol <sup>-1</sup> <sup>a</sup>	ΔH <sup>‡</sup> kcal mol <sup>-1</sup> <sup>a</sup>	ΔS <sup>‡</sup> cal K <sup>-1</sup> mol <sup>-1</sup> <sup>a</sup>
(+) <sub>Tc</sub> -12a	Toluene	90	1.85			
(+) <sub>Tc</sub> -12a	Toluene	100	3.97			
(+) <sub>Tc</sub> -12a	Toluene	110	9.72	22.9	22.2	-24.3
Selenonium ylide <sup>b</sup>	Methanol	80	A <sup>d</sup>			
Selenonium ylide <sup>b</sup>	Methanol	100	B <sup>e</sup>			
Sulfonium ylide <sup>c</sup>	Benzene	25	16.7			

<sup>a</sup> 1 cal = 4.184 J. <sup>b</sup> 1-[4-(-)-Menthylloxycarbonylphenyl(methyl)selenoniumyl]-4,4-dimethyl-2,6-dioxocyclohexan-1-ide, (*R*)-(+)<sub>Sc</sub>-13. <sup>c</sup> Ethylmethylsulfonium benzoylmethylide.<sup>17</sup> <sup>d</sup> No epimerization was observed after 5 days. <sup>e</sup> Thermal decomposition was observed after 2 h by <sup>1</sup>H NMR.<sup>6</sup>

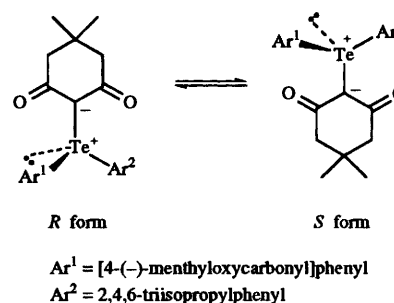
**Fig. 2** Arrhenius plots for the thermal epimerization of (+)<sub>Tc</sub>-12a

optically active telluronium ylide (+)<sub>Tc</sub>-5a was stable at room temperature under atmospheric moisture and was also stable for more than 6 months when kept in a desiccator; *i.e.* no difference was observed in the specific rotation and <sup>1</sup>H NMR spectrum compared with that of the original compound. Similarly, the stability of the telluronium ylide dia.-12a, **b** was examined towards acid, base and water; and the ylide showed the same characteristics under these conditions as for the telluronium ylide dia.-5a, **b**. These results show that these telluronium ylides are stable under atmospheric and basic conditions and unstable under acidic conditions. These properties of the telluronium ylide are similar to those of the sulfonium and selenonium ylides.

#### Epimerization of the optically active telluronium ylides

The kinetics for the thermal epimerization by pyramidal inversion of the optically active telluronium ylides (+)<sub>Tc</sub>-5a and (+)<sub>Tc</sub>-12a were studied. The rate of epimerization by pyramidal inversion of the optically active telluronium ylide was studied by heating a toluene solution of (+)<sub>Tc</sub>-12a in a sealed tube. The decrease of the optical purity calculated from the specific rotation showed a good linear relationship for the first-order rate plots at 90–110 °C. No difference was found in the <sup>1</sup>H NMR spectra of the telluronium ylide before and after the kinetic studies. These results show that the decrease of the specific rotation solely depends on the epimerization and there is no thermal decomposition or hydrolysis during the kinetic studies. The first-order rate constants for the epimerization of compound (+)<sub>Tc</sub>-12a are summarized in Table 1 together with the data for selenonium<sup>6</sup> and sulfonium<sup>17</sup> ylides. Fig. 2 is an Arrhenius plot of the rate constants shown in Table 1. The activation enthalpy and activation entropy for the epimerization from (+)<sub>Tc</sub>-12a to (-)<sub>Tc</sub>-12b were calculated to be 22.9

kcal mol<sup>-1</sup> and -24.3 cal K<sup>-1</sup> mol<sup>-1</sup>, respectively. The rate constants for the epimerization of optically pure selenonium ylide (*R*)-(+)<sub>Tc</sub>-13 could not be determined since thermal decomposition occurred in methanol at 100 °C.<sup>6</sup> The thermal epimerization of (ethylmethylsulfoniumyl)(benzoyl)methanide has been observed at room temperature.<sup>17</sup> These findings show that the telluronium ylide is much more stable than sulfonium and selenonium ylides towards thermal epimerization (racemization by pyramidal inversion) although the substituents on the telluronium ylide employed for this measurement are not the same as those on the sulfonium and the selenonium ylides.



The reason why the telluronium ylide is much more stable than sulfonium and selenonium ylides towards pyramidal inversion is not clear at the present time. We can only qualitatively interpret it as follows. The pyramidal or wedge-shaped structure of telluronium ylide will be sharper than those of sulfonium or selenonium ylides probably because the valence shell electron-pair repulsion in the telluronium ylide is smaller than in the sulfonium or selenonium ylides since the carbon-tellurium bond length is longer than the carbon-sulfur or carbon-selenium bonds and/or because tellurium is less electronegative than sulfur or selenium atoms and therefore the electrons in the C-Te bond lie at a greater distance from the tellurium than they do from the sulfur and selenium in C-S and C-Se bonds, respectively. Accordingly, a higher reaction temperature or activation energy is required for the pyramidal inversion of the telluronium ylide. The absolute value of the activation entropy of the telluronium ylide (+)<sub>Tc</sub>-12a was much greater than that of the sulfonium ylide as shown in Table 1. The large value of the activation entropy for the epimerization of the telluronium ylide (+)<sub>Tc</sub>-12a is also considered to be due to the bulky substituents in the transition state. The kinetics of the epimerization of (+)<sub>Tc</sub>-5a were also examined under similar conditions. However, this compound decomposed faster than the epimerization occurred and therefore rate constants for the epimerization could not be determined.

In conclusion, diastereoisomeric telluronium ylides were optically resolved as stable crystals for the first time. The absolute configurations were determined, and a kinetic study for the epimerization by pyramidal inversion was achieved.

### Experimental

Mps were determined on a Yamato MP-21 melting point apparatus and a Yanako MP-500D micro melting point apparatus, and are uncorrected. IR spectra were determined on a Hitachi 260-10 infrared spectrophotometer and a JASCO FT/IR-5MP Fourier transform infrared spectrophotometer with samples as either neat liquids or KBr disks. UV-VIS spectra were measured on a Shimadzu UV-160A UV-VIS recording spectrophotometer and a UV-3101PC UV-VIS-NIR scanning spectrophotometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{125}\text{Te}$  NMR spectra were determined on a JEOL JNM-EX-400 FT NMR spectrometer at 400, 100 and 126 MHz, respectively. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were referenced to  $\text{Me}_4\text{Si}$  as internal standard and  $J$  values are given in Hz. The  $^{125}\text{Te}$  NMR chemical shifts were referenced to  $\text{Me}_2\text{Te}$  as external standard. Mass spectra were measured on a JEOL JMS-AX505W mass spectrometer with a JMA-DA5000 mass data system by the electron impact (EI) ionizing technique at 20–70 eV. Optical rotations were measured on JASCO DIP-140 and JASCO DIP-370 digital polarimeters and are given in units of  $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$ , and CD spectra were recorded on JASCO J-40A and JASCO J-600 spectrometers. TLC and preparative TLC (PLC) were performed with Merck Art. 5554 DC-Alufolien kieselgel 60 F<sub>254</sub>. Column chromatography was performed with Wakogel C-200 and Daisogel IR-60 (63/210  $\mu\text{m}$ ). HPLC was performed using a Hitachi 655 liquid chromatograph with Daicel silica gel Chiralpack AD and AS columns, Bakerbond chiral silica gel column, and Bakerbond chiralcel OB, OD, OF, OG, OJ, CA-1 cellulose columns. All solvents were distilled and stored under nitrogen.

#### Synthesis of diastereoisomeric 1-{4-[(–)-menthyloxy-carbonyl]-phenyl(methyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-5a, b

A mixture of thionyl chloride (100  $\text{cm}^3$ ) and *p*-iodobenzoic acid (17.3 g, 70.0 mmol) was refluxed for 2 h. After removal of the excess amount of thionyl chloride under reduced pressure, pyridine (100  $\text{cm}^3$ ) was added to the residue at 0 °C. To the stirred solution of the *p*-iodobenzoyl chloride in pyridine was added dropwise a solution of (–)-menthol (10.9 g, 70.0 mmol) in pyridine (100  $\text{cm}^3$ ) over a period of 30 min, and the solution was stirred at room temperature for 24 h. Pyridine was removed under reduced pressure and water was added to the residual oil, and the organic layer was extracted with benzene (200  $\text{cm}^3 \times 3$ ). The combined extracts were washed with water (200  $\text{cm}^3 \times 3$ ), dried over anhydrous magnesium sulfate and then the solvent was removed under reduced pressure. The residual oil was subjected to silica gel chromatography with benzene as eluent to give a viscous yellow oil of (–)-menthyl *p*-iodobenzoate **2** (25.9 g, 96%);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.77–2.13 (18 H, m), 4.92 (1 H, td,  $J$  11.0 and 4.4) and 7.74 and 7.79 (4 H, ABq,  $J$  8.8);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  2950, 2870, 1750, 1590, 1430, 1310, 1175, 1000 and 790;  $m/z$  386 ( $\text{M}^+$ ), 248, 231 and 139.

To a suspension of tellurium powder (12.8 g, 100 mmol) in THF (100  $\text{cm}^3$ ) cooled to –80 °C under nitrogen was added dropwise methyllithium (1.6 mol  $\text{dm}^{-3}$  solution in hexane; 63.0  $\text{cm}^3$ ) over a period of 30 min, and the mixture was allowed to stand to room temperature and stirred for an additional 30 min to give a solution of lithium methanetelluroolate **1**. To the stirred solution of lithium methanetelluroolate **1** cooled to –80 °C was added dropwise a solution of the ester **2** (38.6 g, 100 mmol) in THF (50  $\text{cm}^3$ ) over a period of 30 min, and the solution was allowed to warm at room temperature and stirred for 3 h.<sup>12</sup> Water (100  $\text{cm}^3$ ) was added to the reaction mixture, and the organic layer was extracted with diethyl ether (200  $\text{cm}^3 \times 3$ ). The combined organic extracts were washed with water (200  $\text{cm}^3 \times 3$ ), dried over anhydrous magnesium sulfate and then

concentrated under reduced pressure. Purification of the product by silica gel chromatography with hexane–diethyl ether (70:1) as eluent gave 4-[(–)-menthyloxy-carbonyl]phenyl methyl telluride **3** as a viscous yellow oil (10.4 g, 26%);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.77–2.13 (18 H, m), 2.25 (3 H, s), 4.92 (1 H, td,  $J$  11.0 and 4.4) and 7.65 and 7.85 (4 H, ABq,  $J$  8.3);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  2955, 2928, 2868, 2361, 1711, 1588, 1275, 1115, 1105 and 770;  $m/z$  404 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ), 402 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ), 400 ( $\text{M}^+$ ,  $^{126}\text{Te}$ ), 265, 249 and 139.

To a solution of telluride **3** (5.59 g, 13.9 mmol), pyridine (1.09 g, 13.9 mmol) and methanol (2.23 g, 69.5 mmol) in dichloromethane (300  $\text{cm}^3$ ) was added dropwise a solution of *tert*-butyl hypochlorite (1.51 g, 13.9 mmol) in dichloromethane (80  $\text{cm}^3$ ) over a period of 30 min at –25 °C, and the solution was stirred for an additional 1 h.<sup>13</sup> After confirmation by TLC that the starting telluride **3** had been completely consumed, the reaction mixture was taken up in aq. sodium hydroxide (1.22 g in 80  $\text{cm}^3$ ) and then the organic layer was separated. The aqueous layer was extracted with dichloromethane (30  $\text{cm}^3 \times 3$ ), and the combined organic extracts were washed with water (100  $\text{cm}^3 \times 2$ ) and dried over anhydrous magnesium sulfate. Removal of the solvent and pyridine under reduced pressure (rotary evaporator and then vacuum pump) afforded 4-[(–)-menthyloxy-carbonyl]phenyl methyl telluroxide **4** (5.90 g, 100%);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.77–2.13 (18 H, m), 2.25 (3 H, s), 5.02 (1 H, td,  $J$  11.0 and 4.4) and 7.65 and 7.86 (4 H, ABq,  $J$  8.3);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2970, 2380, 1700, 1280, 1110 and 780. Telluroxide **4** was used immediately in the next reaction since it was unstable under atmospheric conditions.

To a solution containing freshly prepared telluroxide **4** (5.77 g, 13.8 mmol) and dimedone (1.94 g, 13.8 mmol) in chloroform (200  $\text{cm}^3$ ) was added anhydrous magnesium sulfate (1.83 g, 15.2 mmol), and the mixture was stirred for 24 h at room temperature.<sup>11</sup> The magnesium sulfate was filtered off by cellulose short column chromatography using dichloromethane as eluent and the solvent was removed under reduced pressure to give a diastereoisomeric mixture of 1-{4-[(–)-menthyloxy-carbonyl]phenyl(methyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-5a, b (9.02 g, 100%) as colourless crystals; mp 91–95 °C;  $[\alpha]_{\text{D}} -36.3$  (*c* 0.955,  $\text{CHCl}_3$ );  $\delta_{\text{H}}(\text{CDCl}_3)$  0.78–2.11 (18 H, m), 1.10 (6 H, s), 2.34 (4 H, s), 2.74 (3 H, s), 4.90 (1 H, td,  $J$  11.0 and 4.4) and 7.75 and 8.06 (4 H, ABq,  $J$  8.3);  $\delta_{\text{C}}(\text{CDCl}_3)$  16.4, 20.7, 22.0, 23.5, 26.5, 28.6, 31.4, 32.4, 34.2, 40.9, 47.2, 51.1, 75.6, 87.8, 126.3, 131.0, 133.1, 133.6, 164.9 and 193.8;  $\delta_{\text{Tc}}(\text{C}_6\text{D}_6)$  1661 (one isomer) and 1663 (another isomer);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2950, 1705, 1580, 1495, 1280, 1105, 835 and 750;  $m/z$  542 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ), 540 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ), 538 ( $\text{M}^+$ ,  $^{126}\text{Te}$ ), 404, 402, 400, 266, 204, 202, 138, 123, 95, 83 and 69 [Found: *M*, 542.1647 ( $^{130}\text{Te}$ ). Calc. for  $\text{C}_{26}\text{H}_{36}\text{O}_4$   $^{130}\text{Te}$ : *M*, 542.1676; Found: C, 57.3; H, 7.0. Calc. for  $\text{C}_{26}\text{H}_{36}\text{O}_4\text{Te}$ : C, 57.81; H, 6.72%].

#### Synthesis of diastereoisomeric 1-{4-[(–)-menthyloxy-carbonyl]-phenyl(2,4,6-triisopropylphenyl)telluroniumyl}-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-12a, b

To a solution of 2,4,6-triisopropylphenylmagnesium bromide [prepared by the reaction of 1-bromo-2,4,6-triisopropylbenzene (55.5 g, 200 mmol) in THF (120  $\text{cm}^3$ ) with magnesium (4.77 g, 200 mmol) in the presence of a piece of iodine under nitrogen] was added tellurium powder (5.0 g, 40 mmol), and the mixture was heated using a heat gun until the tellurium powder had disappeared completely. Further tellurium powder (20.0 g, 160 mmol) was added gradually to the reaction mixture which was refluxed for an additional 1 h. The reaction mixture was poured into ice-cold dilute hydrochloric acid, and the organic layer was extracted with benzene (200  $\text{cm}^3 \times 3$ ). The combined organic extracts were washed with water (200  $\text{cm}^3 \times 3$ ), dried over magnesium sulfate and then the solvent was removed under

reduced pressure. To the residual oil of 2,4,6-triisopropyl benzenetellurole 6 was added 5 pellets of sodium hydroxide and 99% ethanol (400 cm<sup>3</sup>), and the mixture was stirred under oxygen bubbling for 3 h. Bis(2,4,6-triisopropylphenyl) ditelluride 7 (28.9 g, 45%) was precipitated as dark red crystals; mp 81.6–82.2 °C;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.00 (24 H, d, *J* 6.8), 1.20 (12 H, d, *J* 6.8), 2.84 (2 H, sept., *J* 6.8), 3.52 (4 H, sept., *J* 6.8) and 6.88 (4 H, s); *m/z* 666 ( $\text{M}^+$ , <sup>130</sup>Te), 664 ( $\text{M}^+$ , <sup>128</sup>Te), 662 ( $\text{M}^+$ , <sup>126</sup>Te), 660, 658, 537, 535, 533, 333, 331, 329, 258, 256, 254 and 203.

A solution of ditelluride 7 (19.9 g, 30.0 mmol) in 99% ethanol (300 cm<sup>3</sup>) was heated at reflux for 30 min to dissolve the ditelluride and the solution was cooled to –10 °C. Sodium borohydride (4.32 g, 120 mmol) was added slowly to the solution until the colour of the ditelluride had disappeared to give a solution of sodium 2,4,6-triisopropylbenzenetellurole 8. To the solution of 8 was added slowly 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate<sup>15</sup> (18.2 g, 69.0 mmol) over a period of 30 min, and then the mixture was stirred for an additional 12 h at room temperature. The ethanol was removed under reduced pressure and then water (200 cm<sup>3</sup>) was added to the residue, and the organic layer was extracted with dichloromethane (200 cm<sup>3</sup> × 3). The combined organic extracts were washed with water (200 cm<sup>3</sup> × 3) and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was subjected to the silica gel chromatography with hexane–ethyl acetate (15:1) as eluent to give 4-(ethoxycarbonyl)phenyl 2,4,6-triisopropylphenyl telluride 9 (9.15 g, 32%) as a colourless oil;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.15 (12 H, d, *J* 6.8), 1.29 (6 H, d, *J* 6.8), 1.34 (3 H, t, *J* 6.8), 2.94 (1 H, sept., *J* 6.8), 3.66 (2 H, sept., *J* 6.8), 4.31 (2 H, q, *J* 6.8), 7.11 (2 H, s) and 7.29 and 7.73 (4 H, ABq, *J* 7.3);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.3, 23.9, 24.6, 34.2, 40.2, 60.8, 119.4, 121.8, 126.3, 128.4, 129.8, 133.2, 151.4, 155.1 and 166.6;  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  2960, 2930, 2870, 2124, 1717, 1588, 1460, 1275, 1177, 1105, 1013 and 754; *m/z* 482 ( $\text{M}^+$ , <sup>130</sup>Te), 480 ( $\text{M}^+$ , <sup>128</sup>Te), 478 ( $\text{M}^+$ , <sup>126</sup>Te), 454, 452, 450, 428, 426, 424, 372, 370, 368, 332, 330, 328, 279, 277, 275 and 149.

To a stirred solution of (–)-menthol (7.71 g, 49.4 mmol) in THF (150 cm<sup>3</sup>) was added butyllithium (1.6 mol dm<sup>–3</sup> solution in hexane; 15.2 cm<sup>3</sup>) at –10 °C under nitrogen, and the resulting solution was added to a solution of the ester 9 (11.8 g, 24.7 mmol) in THF (10 cm<sup>3</sup>) at 0 °C.<sup>16</sup> The solution was stirred at room temperature for an additional 3 h and then the THF was removed under reduced pressure, and water (100 cm<sup>3</sup>) was added to the residue. The organic layer was extracted with dichloromethane (50 cm<sup>3</sup> × 3), and the combined organic extracts were washed with water (50 cm<sup>3</sup> × 3) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography with hexane–ethyl acetate (15:1) as eluent to give 4-[(-)-menthyloxycarbonyl]phenyl 2,4,6-triisopropylphenyl telluride 10 (13.5 g, 92%) as a pale yellow oil;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.75–2.10 (18 H, m), 1.17 (12 H, d, *J* 6.8), 1.30 (6 H, d, *J* 6.8), 2.94 (1 H, sept., *J* 6.8), 3.67 (2 H, sept., *J* 6.8), 4.87 (1 H, td, *J* 11.0 and 4.4), 7.12 (2 H, s) and 7.29 and 7.73 (4 H, ABq, *J* 8.5);  $\delta_{\text{C}}(\text{CDCl}_3)$  16.5, 16.6, 20.7, 22.0, 23.7, 25.5, 26.5, 31.4, 32.4, 34.3, 40.9, 47.2, 75.2, 123.4, 129.9, 131.0, 132.0, 134.4, 144.8, 152.5, 154.3 and 165.6;  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  2959, 2928, 2870, 1713, 1586, 1460, 1273, 1179, 1113, 1103, 1011, 787, 754 and 712; *m/z* 592 ( $\text{M}^+$ , <sup>130</sup>Te), 590 ( $\text{M}^+$ , <sup>128</sup>Te), 588 ( $\text{M}^+$ , <sup>126</sup>Te), 454, 452, 450, 437, 435, 433, 332, 330, 328, 203, 138, 105 and 95.

To a solution containing the telluride 10 (12.8 g, 21.7 mmol), pyridine (1.72 g, 21.7 mmol) and methanol (3.47 g, 109 mmol) in dichloromethane (300 cm<sup>3</sup>) was added slowly a solution of *tert*-butyl hypochlorite (2.36 g, 21.7 mmol) in dichloromethane (80 cm<sup>3</sup>) at –25 °C over a period of 30 min. The solution was stirred for an additional 1 h at room temperature.<sup>13</sup> After confirmation by TLC that the starting telluride 10 had been

completely consumed, the reaction mixture was taken up in aq. sodium hydroxide (1.74 g, in 80 cm<sup>3</sup>) and then the organic layer was separated. The organic layer was extracted with dichloromethane (100 cm<sup>3</sup> × 2) and the combined organic layers were dried over anhydrous magnesium sulfate. The solvent and pyridine were removed under reduced pressure using a rotary evaporator and then a vacuum pump gave 4-[(-)-menthyloxycarbonyl]phenyl 2,4,6-triisopropylphenyl telluroxide 11 (13.2 g, 100%); mp 193.2–195.8 °C;  $[\alpha]_{\text{D}} - 34.7$  (*c* 1.07, CHCl<sub>3</sub>);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.76–2.12 (18 H, m), 0.90 (12 H, d, *J* 6.8), 1.22 (6 H, d, *J* 6.8), 2.84 (1 H, sept., *J* 6.8), 3.79 (2 H, sept., *J* 6.8), 4.91 (1 H, td, *J* 11.0 and 4.4), 6.99 (1 H, s, one isomer), 7.00 (1 H, s, another isomer) and 7.66 and 8.01 (4 H, ABq, *J* 7.8);  $\delta_{\text{C}}(\text{CDCl}_3)$  16.6, 20.7, 22.8, 23.8, 25.5, 26.5, 26.6, 31.4, 32.5, 34.3, 40.9, 47.2, 75.2, 123.4, 129.8, 129.9, 131.0, 132.0, 144.6, 152.5, 154.3 and 165.6;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2957, 2928, 2868, 2370, 1717, 1480, 1284, 1269, 1120, 780 and 750; *m/z* 608 ( $\text{M}^+$ , <sup>130</sup>Te), 606 ( $\text{M}^+$ , <sup>128</sup>Te), 604 ( $\text{M}^+$ , <sup>126</sup>Te), 592, 590, 588, 454, 452, 450, 437, 435, 433, 332, 330, 328, 203, 189 and 105.

To a solution of telluroxide 11 (9.72 g, 16.0 mmol) and dimedone (2.25 g, 16.0 mmol) in chloroform (200 cm<sup>3</sup>) was added anhydrous magnesium sulfate (2.12 g, 17.2 mmol), and the mixture was stirred at room temperature for 24 h.<sup>11</sup> The magnesium sulfate was filtered off by cellulose column chromatography with dichloromethane as eluent and then the solvent was removed under reduced pressure to give a diastereoisomeric mixture of 1-[4-[(-)-menthyloxycarbonyl]phenyl(2,4,6-triisopropylphenyl)telluroniumyl]-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia. -12a, b (11.7 g, 100%) as colourless crystals; mp 115–119 °C;  $[\alpha]_{\text{D}} - 25.4$  (*c* 1.11, CHCl<sub>3</sub>);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.76–2.53 (18 H, m), 0.91 (12 H, d, *J* 6.8), 1.14 (6 H, s), 1.26 (6 H, d, *J* 6.8), 2.34 (4 H, s), 2.91 (1 H, sept., *J* 6.8), 3.34 (2 H, sept., *J* 6.8), 4.90 (1 H, td, *J* 11.0 and 4.4), 7.11 (1 H, s, one isomer), 7.12 (1 H, s, another isomer) and 7.68 and 8.00 (4 H, ABq, *J* 8.7);  $\delta_{\text{C}}(\text{CDCl}_3)$  16.5, 20.8, 22.0, 23.8, 25.4, 26.5, 28.7, 29.7, 31.4, 32.7, 34.2, 36.4, 40.9, 47.2, 51.3, 75.4, 89.8, 123.9, 124.7, 127.1, 130.4, 132.6, 134.3, 153.3, 153.8, 165.2 and 192.3;  $\delta_{\text{T}_e}(\text{C}_6\text{D}_6)$  1724;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2959, 2930, 2870, 1717, 1609, 1593, 1522, 1460, 1387, 1366, 1288, 1269, 1115, 1105, 1010 and 750; *m/z* 730 ( $\text{M}^+$ , <sup>130</sup>Te), 728 ( $\text{M}^+$ , <sup>128</sup>Te), 726 ( $\text{M}^+$ , <sup>126</sup>Te), 592, 590, 454, 452, 450, 368, 203, 149, 147, 145, 138, 129, 127, 125, 105, 83 and 69 (Found: C, 65.6; H, 7.9. Calc. for C<sub>40</sub>H<sub>56</sub>O<sub>4</sub>Te: C, 65.95; H, 7.75%).

#### Optical resolution of telluronium ylides dia. -5a, b and dia. -12a, b

A solution containing a diastereoisomeric mixture (5.7 g) of 1-[4-[(-)-menthyloxycarbonyl]phenyl(methyl)telluroniumyl]-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia. -5a, b  $[\alpha]_{\text{D}} - 36.3$  (*c* 0.955, CHCl<sub>3</sub>) was optically resolved by fractional recrystallization from hexane–dichloromethane (5:1). The specific rotation of the crystalline telluronium ylide did not change after a further five fractional recrystallizations  $\{(+)_{\text{T}_e}\text{-5a}$ ; isolated 0.12 g;  $[\alpha]_{\text{D}} - 7.9$  (*c* 0.205, CHCl<sub>3</sub>), and the other diastereoisomer  $(-)_{\text{T}_e}\text{-5b}$  was obtained from the mother liquor  $\{(-)_{\text{T}_e}\text{-5b}$ ; isolated 3.6 g;  $[\alpha]_{\text{D}} - 38.3$  (*c* 1.06, CHCl<sub>3</sub>)}. The optical purities of  $(+)_{\text{T}_e}\text{-5a}$  and  $(-)_{\text{T}_e}\text{-5b}$  were determined to be 30 and 2% de, respectively, from the <sup>1</sup>H NMR spectra in the absence and presence of a shift reagent, (*S*)-(–)-1'-bi-2-naphthol. We tried to raise the optical purity of ylides  $(+)_{\text{T}_e}\text{-5a}$  and  $(-)_{\text{T}_e}\text{-5b}$  using a number of mixed solvent systems, however, we could not resolve and obtain optically pure diastereoisomers since the solubilities of  $(+)_{\text{T}_e}\text{-5a}$  and  $(-)_{\text{T}_e}\text{-5b}$  differed only slightly.

† Only one <sup>125</sup>Te NMR signal was observed for a diastereoisomeric mixture of telluronium ylide dia.-(+)<sub>T<sub>e</sub></sub>-12a, b in contrast to the case for dia. -5a, b.

Similarly, a solution containing a diastereoisomeric mixture (9.1 g) of 1-[4-[(–)-menthyloxycarbonyl]phenyl(2,4,6-triisopropylphenyl)telluroniumyl]-4,4-dimethyl-2,6-dioxocyclohexan-1-ide dia.-12a, b  $\{[\alpha]_D -25.4$  ( $c$  1.11,  $\text{CHCl}_3$ ) $\}$  was fractionally recrystallized from hexane–dichloromethane (5:1). In spite of our efforts to resolve and isolate optically pure diastereoisomer dia.-12a or dia.-12b, we could not isolate optically pure diastereoisomers, and obtained (+)<sub>Te</sub>-12a as crystals {isolated 0.43 g; mp 150–153 °C;  $[\alpha]_D -8.8$  ( $c$  0.293,  $\text{CHCl}_3$ ); de 25%} and (–)<sub>Te</sub>-2b from the mother liquor {isolated 1.9 g;  $[\alpha]_D -32.3$  ( $c$  1.28,  $\text{CHCl}_3$ ); de 2%}.

Compound (+)<sub>Te</sub>-5a: mp 153–157 °C;  $[\alpha]_D -7.9$  ( $c$  0.205,  $\text{CHCl}_3$ );  $\lambda_{\text{max}}$ (MeOH)/nm 252 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} 1.50 \times 10^4$ ); CD(MeOH)/nm 277 ( $[\theta]/\text{mol}^{-1} \text{ cm}^{-1} +6.11 \times 10^2$ ) and 239 ( $[\theta] +4.94 \times 10^3$ );  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 0.78–2.11 (18 H, m), 1.10 (6 H, s), 2.34 (4 H, s), 2.74 (3 H, s), 4.90 (1 H, td,  $J$  11.0 and 4.4) and 7.75 and 8.06 (4 H, ABq,  $J$  8.3);  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  2950, 1710, 1600, 1515, 1265, 1115 and 750;  $m/z$  542 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ), 540 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ), 538 ( $\text{M}^+$ ,  $^{126}\text{Te}$ ), 404, 402, 400, 266, 204, 202, 138, 123, 95, 83 and 69 [Found:  $M$ , 542.1647 ( $^{130}\text{Te}$ ). Calc. for  $\text{C}_{26}\text{H}_{36}\text{O}_4$   $^{130}\text{Te}$ :  $M$ , 542.1676].

Compound (+)<sub>Te</sub>-12a: mp 150–153 °C;  $[\alpha]_D -8.8$  ( $c$  0.293,  $\text{CHCl}_3$ );  $\lambda_{\text{max}}$ (MeOH)/nm 243 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} 2.58 \times 10^4$ ); CD(MeOH)/nm 293 ( $[\theta]/\text{mol}^{-1} \text{ cm}^{-1} -1.50 \times 10^4$ ) and 270 ( $[\theta] +2.56 \times 10^4$ );  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 0.76–2.53 (18 H, m), 0.91 (12 H, d,  $J$  6.8), 1.14 (6 H, s), 1.26 (6 H, d,  $J$  6.8), 2.34 (4 H, s), 2.91 (1 H, sept.,  $J$  6.8), 3.34 (2 H, sept.,  $J$  6.8), 4.90 (1 H, td,  $J$  11.0 and 4.4), 7.11 (0.75 H, s, one isomer), 7.12 (1.25 H, s, another isomer) and 7.68 and 8.00 (4 H, ABq,  $J$  8.73);  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  2915, 1700, 1585, 1500, 1250, 1105 and 740;  $m/z$  730 ( $\text{M}^+$ ,  $^{130}\text{Te}$ ), 728 ( $\text{M}^+$ ,  $^{128}\text{Te}$ ), 726 ( $\text{M}^+$ ,  $^{126}\text{Te}$ ), 592, 590, 454, 452, 450, 368, 203, 149, 147, 145, 138, 129, 127, 125, 105, 83 and 69 (Found:  $C$ , 66.5;  $H$ , 8.15. Calc. for  $\text{C}_{40}\text{H}_{56}\text{O}_4\text{Te}$ :  $C$ , 65.95;  $H$ , 7.75%).

#### Attempts to separate compounds dia.-5a, b or dia.-12a, b by HPLC using an optically active column

A diastereoisomeric mixture of telluronium ylides dia.-5a, b or dia.-12a, b was subjected to HPLC using optically active silica gel columns such as Daicel Chiralpak AS and AD and Bakerbond chiral column, and optically active cellulose columns such as Bakerbond Chiralcel OB, OD, OF, OG, OJ and CA-1. The solvent system used as eluent was hexane–propan-2-ol (9:1). However, in contrast to our expectations, diastereoisomers dia.-5a, b or dia.-12a, b could not be separated under the conditions employed.

#### Kinetic studies on the epimerization of optically active telluronium ylide (+)<sub>Te</sub>-12a

A solution containing compound (+)<sub>Te</sub>-12a {50.0 mg;  $[\alpha]_D -12.0$  ( $c$  1.02,  $\text{CHCl}_3$ ) $\}$  in toluene (5.0  $\text{cm}^3$ ) was heated at 90, 100 and 110 °C. The specific rotation was measured at adequate time intervals, and the rates for epimerization by pyramidal inversion were plotted to a first-order rate equation. The activation parameters were calculated by Arrhenius and Eyring absolute kinetic equations. The  $^1\text{H}$  NMR spectra of compound

(+)<sub>Te</sub>-12a were the same before and after the kinetic studies, and this means that only pyramidal inversion is occurring under the reaction conditions. On the other hand, compound (+)<sub>Te</sub>-5a decomposed when a toluene solution of (+)<sub>Te</sub>-5a was heated at 80 °C (the  $^1\text{H}$  NMR was complex which shows that decomposition was occurring under the reaction conditions). Thus, we could not determine the rate for the epimerization of optically active compound (+)<sub>Te</sub>-5a.

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