Synthesis and Stability of Optically Active Benzylmethylphenyltelluronium Salts

Toshio Shimizu,* Yoko Azami, Ryuuya Sakurai, Kazunori Hirabayashi, and Nobumasa Kamigata
Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University,
1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397

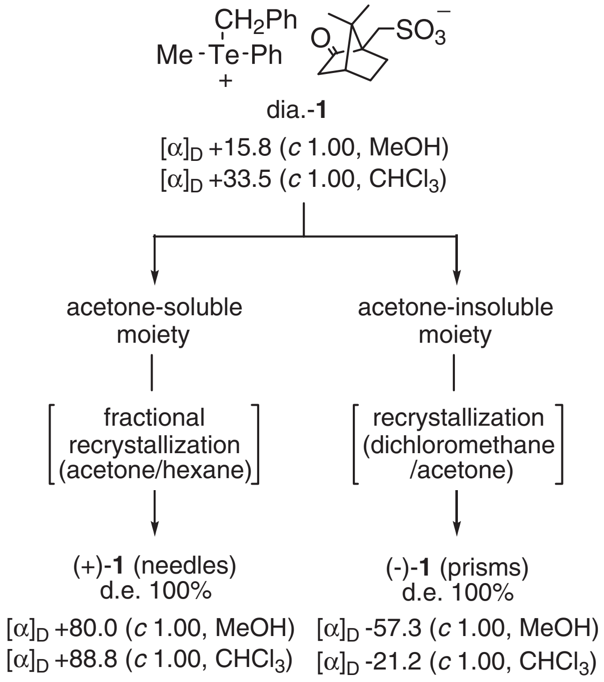
(Received August 26, 2009; CL-090784; E-mail: shimizu-toshio@tmu.ac.jp)

Diastereomeric benzylmethylphenyltelluronium salt was synthesized and optically resolved into the respective optical isomers. The absolute configurations of the isomers were determined by X-ray analysis of the (−)-isomer. Enantiomeric telluronium salts were also obtained by anion-exchange reactions of the diastereomeric isomers. Optically active telluronium bromide was found to racemize in solution and the racemization was indicated to occur through the elimination of benzyl bromide.

A number of optically active tellurium compounds have been synthesized and their properties and reactivities studied.[1,2] Among those, optically active telluronium salts were isolated for the first time by Lowry and Gilbert in 1929,[3] and the next report did not appear until 1945.[4] In those papers, it was described that chiral telluronium salts racemized or decomposed in solution. Previously, we isolated optically active dialkylaryltelluronium salts, however, no racemization was observed even in solution.[5–7] Koizumi and co-workers also isolated stable optically active dialkyl- or alkylaryl(2-*exo*-hydroxy-10-bornyl)telluronium salts.[8] Recently, we synthesized diastereomeric benzylmethylphenyltelluronium salt and succeeded to resolve it into the optical isomers. Optically active benzylmethylphenyltelluronium bromide prepared from the diastereomeric isomer was found to racemize in solution, and the racemization was estimated to occur via the formation of achiral methyl phenyl telluride with the elimination of benzyl bromide.

Benzylmethylphenyltelluronium bromide **3** was prepared from methyl phenyl telluride[9] and benzyl bromide in 87% yield. A diastereomeric sample of benzylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate (dia.-**1**)[10] was synthesized in 94% yield by anion-exchange reaction of the bromide with silver (1*S*)-(+)-camphor-10-sulfonate. The diastereomeric mixture dia.-**1** was resolved into an acetone-soluble moiety and an acetone-insoluble moiety. Repeated recrystallization (4 times) of the soluble moiety from acetone/hexane gave the diastereomerically pure (+)-telluronium salt (+)-**1** as colorless needles (Scheme 1). On the other hand, crystallization (once) of the acetone-insoluble moiety from dichloromethane/acetone yielded the diastereomerically pure (−)-telluronium salt (−)-**1** as colorless prisms.

The stereochemistry of the tellurium atom of (−)-**1** was determined to be S on the basis of X-ray crystallographic analysis (Figure 1).[11] Therefore, the configuration of (+)-**1** was assigned to be R around the tellurium atom. The tellurium atom of (*S*)-(−)-**1** was found to interact with two oxygen atoms of different sulfonate anions with distances of 2.84 and 3.02 Å, respectively, in the crystalline state.



Scheme 1. Optical resolution of diastereomeric benzylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate (dia.-**1**).

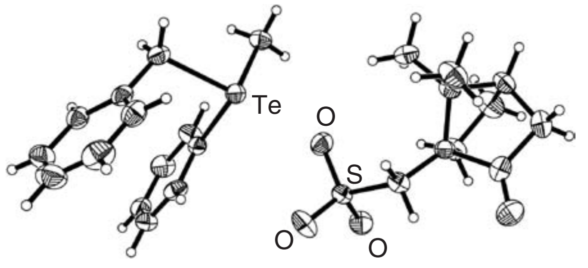
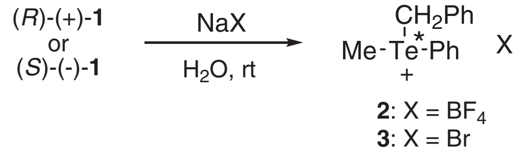


Figure 1. ORTEP drawing of (*S*)-(−)-**1**.

To obtain enantiomeric telluronium salts, anion-exchange reactions were examined. Enantiomeric (*R*)-(+)- and (*S*)-(−)-benzylmethylphenyltelluronium tetrafluoroborates {(*R*)-(+)-**2** and (*S*)-(−)-**2**} were isolated in 60 and 65% yields, respectively, by reacting (*R*)-(+)-**1** and (*S*)-(−)-**1** with sodium tetrafluoroborate (Table 1). The optical purities were determined to be 100% ee, respectively, on the basis of ^{1}H NMR measurements by using (*S*)-(−)-1,1′-bi-2-naphthol as a chiral shift reagent. Enantiomerically pure (*R*)-(+)- and (*S*)-(−)-benzylmethylphenyltelluronium bromides {(*R*)-(+)-**3** and (*S*)-(−)-**3**} were also obtained by similar anion-exchange reactions.

Diastereomeric telluronium salt (*R*)-(+)-**1** showed a positive first Cotton effect at 298 nm and a positive second Cotton effect at 247 nm on the circular dichroism spectrum in methanol

Table 1. Anion-exchange reactions of (*R*)-(+)-**1** and (*S*)-(−)-**1**



2: X = BF_4
3: X = Br

Compound	Yield	$[\alpha]_D$[a]	
		in MeOH	in $CHCl_3$
(*R*)-(+)-**2**	60	+96.3	+143.5
(*S*)-(−)-**2**	65	−94.1	−158.3
(*R*)-(+)-**3**	67	+76.5[b]	+105.6[b]
(*S*)-(−)-**3**	80	−77.3	−107.4

[a] Specific rotations were measured at 25 °C and $c = 1.00$. [b] $c = 0.50$.

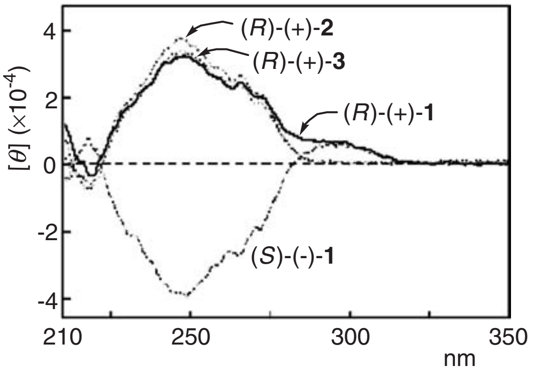


Figure 2. Circular dichroism spectra of optically active telluronium salts **1**–**3** in methanol.

(Figure 2). On the other hand, telluronium salt (*S*)-(−)-**1** also showed a similar positive Cotton effect at 297 nm while the corresponding second Cotton effect was negative. Therefore, the positive first Cotton effects of (*R*)-(+)-**1** and (*S*)-(−)-**1** were found to be derived from the common chiral counter anion, (1*S*)-(+)-camphor-10-sulfonate, and the second Cotton effect must be derived from the chirality of the tellurium atoms. Enantiomeric telluronium salts (*R*)-(+)-**2** and (*R*)-(+)-**3** also showed a positive Cotton effect around 247 nm in methanol similar to that of (*R*)-(+)-**1**, and the (*S*)-(−)-isomers showed symmetrical spectra to the (*R*)-(+)-isomers, respectively.

Telluronium salts (*S*)-(−)-**1** and (*S*)-(−)-**2** were stable both in the crystalline state and in solution. However, racemization of (*S*)-(−)-**3** was observed in both chloroform and methanol. These results demonstrate that telluronium salts possessing counter anions with high nucleophilicity racemize in solution. The racemization of (*S*)-(−)-**3** obeyed first-order kinetics, and the first-order rate constants k and half-lives $t_{1/2}$ in chloroform and methanol were $6.10 \times 10^{-3}\,s^{-1}$ (1.9 h) and $2.99 \times 10^{-4}\,s^{-1}$ (39 h), respectively. The results show that the racemization is faster in less polar solvents. When the reaction of racemic benzylmethylphenyltelluronium bromide **3** with *p*-methylbenzyl bromide was carried out in chloroform-*d* at room temperature, methyl(*p*-methylbenzyl)phenyltelluronium bromide was obtained together with benzyl bromide and a small amount of methyl phenyl telluride. Therefore, the racemization is speculated to proceed as below. The counter anion attacks the positive tellurium atom of the telluronium salt to give a tellurane. The tellurane yields telluride and benzyl bromide via the ligand coupling reaction, and then telluronium salt would be reproduced as a racemate. Details of the mechanism are under investigation.

References and Notes

1 For books see: a) T. Shimizu, N. Kamigata, in *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*, ed. by F. A. Devillanova, RSC, Cambridge, **2007**, p. 577. b) *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. by S. Patai, Z. Rappoport, Wiley, New York, **1987**, Vol. 2. c) C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press, Oxford, **1986**.

2 For reviews see: a) M. Tiecco, L. Testaferri, F. Marini, L. Bagnoli, C. Santi, A. Temperini, S. Sternativo, C. Tomassini, *Phosphorus, Sulfur Silicon Relat. Elem.* **2005**, *180*, 729. b) S. Uemura, *Phosphorus, Sulfur Silicon Relat. Elem.* **2001**, *171*, 13. c) Y. Nishibayashi, S. Uemura, *Topics in Current Chemistry*, Springer, **2000**, Vol. 208, pp. 201, 235. d) T. Shimizu, N. Kamigata, *Rev. Heteroatom Chem.* **1998**, *18*, 11. e) T. Shimizu, N. Kamigata, *Org. Prep. Proced. Int.* **1997**, *29*, 603. f) Y. Nishibayashi, S. Uemura, *Rev. Heteroatom Chem.* **1996**, *14*, 83. g) N. Komatsu, S. Uemura, *Advances in Detailed Reaction Mechanisms*, **1995**, Vol. 4, p. 73. h) S. Tomoda, Y. Usuki, K. Fujita, M. Iwaoka, *Rev. Heteroatom Chem.* **1991**, *4*, 249.

3 T. M. Lowry, F. L. Gilbert, *J. Chem. Soc.* **1929**, 2867.

4 F. G. Holliman, F. G. Mann, *J. Chem. Soc.* **1945**, 37.

5 T. Shimizu, T. Urakubo, N. Kamigata, *Chem. Lett.* **1996**, 297.

6 T. Shimizu, T. Urakubo, N. Kamigata, *J. Org. Chem.* **1996**, *61*, 8032.

7 T. Shimizu, T. Urakubo, P. Jin, M. Kondo, S. Kitagawa, N. Kamigata, *J. Organomet. Chem.* **1997**, *539*, 171.

8 J. Zhang, S. Saito, T. Koizumi, *J. Org. Chem.* **1998**, *63*, 5423.

9 E. G. Hope, T. Kemmitt, W. Levason, *Organometallics* **1988**, *7*, 78.

10 Supporting Information (NMR data) is available free of charge on the web at http://www.csj.jp/journals/chem-lett/index.html.

11 Crystal data for (*S*)-(−)-**1**: Compound (*S*)-(−)-**1** crystallized in the monoclinic space group $P2_1$, with $a = 7.0953(12)$, $b = 12.039(4)$, $c = 13.497(3)$ Å, $\beta = 91.077(9)°$, $V = 1152.7(5)$ Å^3, $Z = 2$, and $D_{calcd} = 1.562\,g\,cm^{-3}$. 5123 data collected with Mo Kα radiation ($\lambda = 0.71075$ Å) and $F_o > 2.0\sigma(F_o)$ were used in the least-squares refinement to yield $R = 2.3\%$, $R_w = 4.8\%$. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-747370. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).