

## A Systematic $^{125}\text{Te}$ NMR Study of Organotellurium Compounds: The Effect of Oxidation States and Substituents

Shinichi Saito,<sup>\*,†</sup> Jian Zhang, Kyoko Tanida, Shigemasu Takahashi and Toru Koizumi<sup>\*,‡</sup>

*Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama, 930-0194, Japan*

Received 1 December 1998; accepted 8 January 1999

**Abstract:**  $^{125}\text{Te}$  NMR spectra of aromatic and aliphatic organotellurium compounds were observed in order to investigate the relationship between the structure and the  $^{125}\text{Te}$  NMR chemical shift of the compounds. The  $^{125}\text{Te}$  NMR chemical shift of organotellurium compounds is sensitive to the type and size of the substituents (aromatic, aliphatic) and the oxidation state of the Te atom. The chemical shift of halooxatelluranes moved *upfield* when an electron-withdrawing group was attached to the phenyl group. The observed results could be interpreted in terms of the resonance structures of the halooxatelluranes. © 1999 Elsevier Science Ltd. All rights reserved.

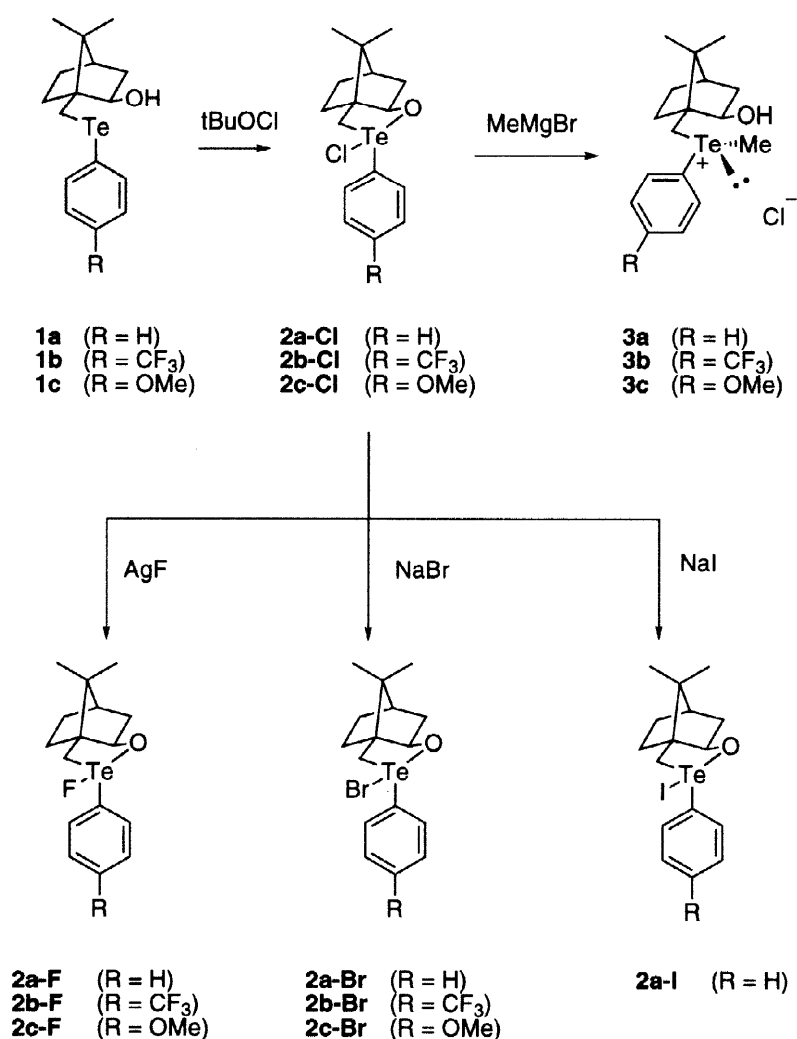
**Keywords:** Organotellurium compounds,  $^{125}\text{Te}$  NMR, Electronic effects

$^{125}\text{Te}$  NMR spectroscopy is a powerful tool for obtaining structural information on organotellurium compounds.<sup>1</sup>  $^{125}\text{Te}$  NMR spectra could be easily observed due to the high natural abundance, short  $T_1$  relaxation time, and the range of the chemical shift is rather wide (3500 ppm), which is advantageous for distinguishing the Te atoms in different chemical environments. In some studies, the chemical shifts are shown to correlate with the oxidation states of the Te atom and the electronegativity of the ligands.<sup>2</sup> For example, Zumbulyadis and Gysling reported that the increase in oxidation states causes the low field shift of the  $^{125}\text{Te}$  NMR chemical shift.<sup>2a</sup> On the other hand, Gassmann and Detty et al. did not observe this tendency when they observed the  $^{125}\text{Te}$  NMR spectra of telluropyranes and related compounds.<sup>2i</sup> Further study is required to understand the relationship between the structure of organotellurium compounds and the  $^{125}\text{Te}$  NMR chemical shifts. In this paper, we report the electronic effect on the  $^{125}\text{Te}$  NMR chemical shifts of a series of Te(II) and Te(IV) compounds such as organotellurides, halooxatelluranes and organotellurium salts.

## Results

The aromatic organotellurium compounds were prepared as described earlier by our group (Scheme 1). Thus, organotellurides (**1a-c**) were prepared by the reaction of (1S)-10-bromo-2-*exo*-borneol with diaryl (or dialkyl) ditelluride, and the tellurides were treated with *t*BuOCl to yield chlorotelluranes.<sup>3</sup> Chlorotelluranes were converted to other halotelluranes by halogen exchange reaction.<sup>4</sup> Telluronium salts (**3a-c**) were prepared by the reaction of halotelluranes with Grignard reagents.<sup>5</sup> A substituted phenyl group was attached to the tellurium atom in order to study the electronic effect on the chemical shift. The proton-decoupled <sup>125</sup>Te NMR spectra were observed and referenced to external diphenyl ditelluride in CH<sub>2</sub>Cl<sub>2</sub> ( $\delta$  422 ppm, relative to dimethyl telluride  $\delta$  0 ppm).<sup>6</sup> The <sup>125</sup>Te NMR chemical shifts of the aromatic organotellurium compounds are summarized in Table 1.

**Scheme 1**



**Table 1.**  $^{125}\text{Te}$  NMR spectroscopic data for aromatic organotellurium compounds (**1-3**).

entry	class of the substrate	compound	chemical shift (ppm)
1	telluride	<b>1a</b>	363
2		<b>1b</b>	376
3		<b>1c</b>	350
4	tellurane	<b>2a-F</b>	1871 <sup>a</sup>
5		<b>2b-F</b>	1866 <sup>b</sup>
6		<b>2c-F</b>	1877 <sup>c</sup>
7		<b>2a-Cl</b>	1841
8		<b>2b-Cl</b>	1833
9		<b>2c-Cl</b>	1847
10		<b>2a-Br</b>	1860
11		<b>2b-Br</b>	1854
12		<b>2c-Br</b>	1868
13		<b>2a-I</b>	1876
14	telluronium salt	<b>3a</b>	564 (606) <sup>d,e</sup>
15		<b>3b</b>	621 <sup>d</sup>
16		<b>3c</b>	533

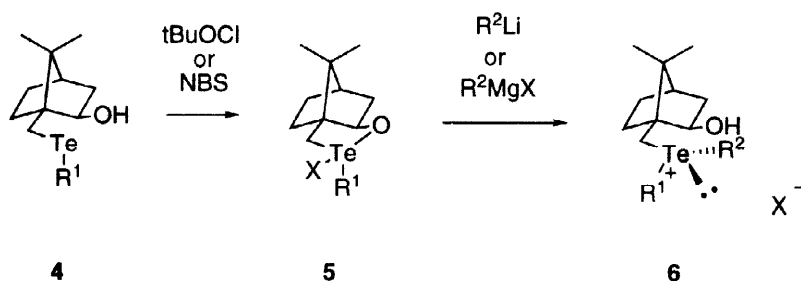
<sup>a</sup> Doublet,  $J_{\text{Te-F}} = 754$  Hz. <sup>b</sup> Doublet,  $J_{\text{Te-F}} = 699$  Hz. <sup>c</sup> Doublet,  $J_{\text{Te-F}} = 766$  Hz. <sup>d</sup> In  $\text{CD}_3\text{OD}$ . <sup>e</sup> Ref. 5b.

The chemical shifts of aromatic Te(II) compounds (tellurides, **1a-c**) were ca. 350 ppm, and they are affected by the substituents attached to the Te atom. As expected, the  $^{125}\text{Te}$  NMR chemical shift moved downfield in the presence of an electron-withdrawing group attached to the benzene ring. When the tellurides were converted to halooxatellurane, the chemical shifts moved downfield (1800 - 1900 ppm). The chemical shift is affected by the halogen atom attached to the tellurium atom, and the substituent attached to the phenyl group. When a heavier halogen atom, except for the fluorine atom, was attached to the tellurium atom, the chemical shift moved downfield. It is noteworthy that the coupling between the fluorine atom and the tellurium atom was observed (Table 1, entries 4-6).<sup>7</sup> The coupling constant was smaller when an electron-withdrawing group is attached to the benzene ring. The chemical shifts of the chlorooxatelluranes moved slightly *downfield* in the presence of an electron-donating group attached to the phenyl ring. Similar results were obtained by observing the  $^{125}\text{Te}$  NMR chemical shifts of the corresponding fluoro- and bromooxatelluranes. This trend is in contrast to the results we report in this paper for other organotellurium compounds such as tellurides (*vide supra*) and telluronium salts (*vide infra*).

The chemical shifts of the telluronium salts moved upfield compared to those of the parent halooxatelluranes (500 - 600 ppm). As is the case for the chemical shifts of the tellurides, the chemical shift is correlated with the substituents attached to the Te atom. Thus, an electronegative group attached to the phenyl group caused the low field shift of the  $^{125}\text{Te}$  NMR chemical shift.

We also prepared a series of aliphatic organotellurium compounds (Scheme 2)<sup>3-5</sup> and observed the  $^{125}\text{Te}$  NMR spectra (Table 2). The chemical shifts of the aliphatic tellurides (Table 2, entries 1-2) were observed at lower fields compared to those of the aromatic tellurides (Table 1, entries 1-3). On the other hand, the chemical shifts of the aliphatic halooxatelluranes were similar to those of aromatic halotelluranes (Table 2, entries 3-7), and they were also affected by the halogen atom directly attached to the tellurium atom. As shown in Table 2 (entries 8-14), the  $^{125}\text{Te}$  NMR chemical shifts of telluronium salts range from 440 ppm to 500 ppm, and the value was sensitive to the substituent attached to the tellurium atom: even the  $^{125}\text{Te}$  NMR chemical shifts of the diastereomeric compounds were significantly different (Table 2, entries 9-12). It is also noteworthy that the

Scheme 2



**Table 2.**  $^{125}\text{Te}$  NMR spectroscopic data for aliphatic organotellurium compounds (4-6).

entry	class of compounds	compound	R <sup>1</sup>	R <sup>2</sup>	X	chemical shift (ppm)
1	telluride	<b>4a</b>	Me	-	-	628
2		<b>4b</b>	Et	-	-	812
3	tellurane	<b>5a</b>	Me	-	Br	1798
4		<b>5b</b>	Et	-	Cl	1852
5		<b>5c</b>	Et	-	Br	1865
6		<b>5d</b>	n-Bu	-	Cl	1838
7		<b>5e</b>	n-Bu	-	Br	1851
8	telluronium salt	<b>6a</b>	Me	Me	Cl	440 <sup>a</sup>
9		<b>6b</b>	Me	Et	Cl	498 <sup>a</sup>
10		<b>6c</b>	Et	Me	Cl	488 <sup>a</sup>
11		<b>6d</b>	Me	Et	Br	499 <sup>a</sup>
12		<b>6e</b>	Et	Me	Br	485 <sup>a</sup>
13		<b>6f</b>	Me	n-Bu	Cl	481 <sup>a</sup>
14		<b>6g</b>	n-Bu	Me	Cl	477 <sup>a</sup>

<sup>a</sup> Ref. 5b.

chemical shift of the cationic telluronium salt was *upfield* compared to the neutral tellurides (Table 2, entries 1-2 and 9-14). On the other hand, the effect of the counter anion on the  $^{125}\text{Te}$  NMR chemical shift was small (Table 2, entries 9-12).

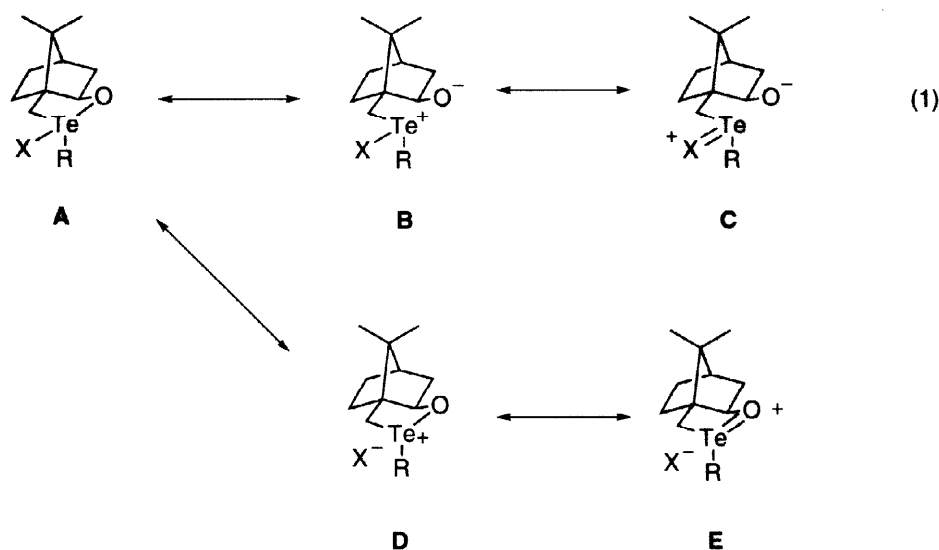
## Discussion

Though the relationship between the structure and the  $^{125}\text{Te}$  NMR chemical shift of organotellurium compounds has been studied by some research groups, the interpretation of the results is not easy. As is well known,<sup>1</sup> and also found in the present work, the  $^{125}\text{Te}$  NMR chemical shift of aromatic organotellurium compounds is different from that of aliphatic organotellurium compounds. We discuss the results of the observed  $^{125}\text{Te}$  NMR chemical shift of aliphatic tellurium compounds and aromatic tellurium compounds separately.

The chemical shifts of aliphatic tellurides were downfield compared to those of aromatic tellurides. The result is not in accordance with the order generally observed,<sup>1</sup> and we assume that the chemical shift of aliphatic tellurides (**4a-b**) moved downfield due to the presence of the bulky 2-*exo*-hydroxy-10-bornyl group. The electronic structure of some tellurium compounds may be affected by a large substituent. In fact, McFarlane et al. reported that the  $^{125}\text{Te}$  NMR chemical shift of  $i\text{Pr}_2\text{Te}$  (707 ppm) moved significantly downfield compared to that of  $\text{Me}_2\text{Te}$  (0 ppm).<sup>2b</sup> On the other hand, the chemical shift of the aromatic tellurides was scarcely affected by the size of the substituent: the chemical shift of **1a** (363 ppm) is comparable to the chemical shift of  $\text{PhTeMe}$  (330 ppm),<sup>2b</sup> and the effect of the bulky substituent is limited. The chemical shift of the aromatic tellurides moved downfield in the presence of an electron-withdrawing group, and it is possible to explain this result in terms of the decreased shielding effect on the tellurium nucleus.

Compared to other organotellurium compounds we investigated, the difference between the chemical shifts of aromatic and aliphatic halooxatellurane was small. The range of the chemical shift was quite similar (1800-1900 ppm; see Table 1, entries 4-13, and Table 2, entries 3-6), and the chemical shift moved downfield when a heavier halogen atom was attached to the tellurium atom. The observed tendency is not in accordance with the results reported for the chemical shift of dihalotelluranes ( $\text{R}_2\text{TeX}_2$ , X = halogen); the values of the chemical shifts increase in the series  $\text{I} < \text{Br} < \text{Cl} < \text{F}$  for dihalotelluranes<sup>2a,2h</sup> and trihalotelluranes,<sup>9</sup> while the value of the chemical shift of halooxatelluranes increase in the series  $\text{Cl} < \text{Br} < \text{F} < \text{I}$  (Table 1, entries 4-13). We also observed an unusual effect of the substituent attached to the phenyl group of aromatic halooxatelluranes; the attachment of an electronegative substituent (i. e., more electronegative halogen atom, except for fluorine atom, or more electronegative phenyl group) to a halooxatellurane caused the upfield shift of the  $^{125}\text{Te}$  NMR spectrum.<sup>9</sup> It would be possible to explain the current results by considering the resonance structure of the halooxatelluranes and the electronegativity of the halogen atom and oxygen atom (eq. 1). The polarity of the X-Te-O bond will correlate with the  $^{125}\text{Te}$  NMR chemical shift, and if the X-Te-O bond becomes more polar, the  $^{125}\text{Te}$  NMR chemical shift will move downfield.<sup>10</sup> The resonance structures B and C would become important when a chlorine (electronegativity value (EN) = 3.16), bromine (EN = 2.96), or iodine atom (EN = 2.66) was bound to the Te atom, since they are less electronegative compared to oxygen atom (EN = 3.44).<sup>12</sup> Less electronegative atoms will stabilize the ionic resonance structures B and C, and hence the low field shift of  $^{125}\text{Te}$  NMR signal will be observed. The exceptional spectral behavior (low field shift) of fluorooxatelluranes may be explained in terms of the high electronegativity of the fluorine atom (EN = 3.98) compared to that of the

oxygen atom; if a fluorine atom is attached to the Te atom, the resonance structures D and E might also become important structures to some extent, and it may cause the low field shift.<sup>12</sup>



The effect of substituents attached to the phenyl ring on the  $^{125}\text{Te}$  NMR chemical shift could be interpreted similarly. Thus, when the electron-withdrawing ability of a substituent attached to the equatorial position of the tellurium atom increases, the contribution of the ionic resonance structures B and C decreases, and the high field shift of  $^{125}\text{Te}$  NMR chemical shift would be observed. If an electron-donating group is attached to the phenyl group, the X-Te-O bond will be more polar due to the stabilization of the resonance structures B and C, and the low field shift of  $^{125}\text{Te}$  NMR signal would be observed.

It is noteworthy that the values of the chemical shift of aliphatic telluronium salts are smaller than those of aliphatic tellurides. This result may be interpreted in terms of the unusual low field shift of the aliphatic telluride in the presence of a bulky substituent. Unlike the chemical shifts of tellurides, the chemical shifts of organotelluronium salts are not seriously affected by the bulkiness of the attached substituents: the  $^{125}\text{Te}$  NMR chemical shift of **3a** (564 ppm) was comparable to those of ethylmethylphenyltelluronium salts (560–610 ppm),<sup>2j</sup> and the chemical shift of **6a** (440 ppm) was not so different from that of dimethylethyltelluronium bromide (470 ppm).<sup>2f</sup> The chemical shift of the aromatic telluronium salts moved downfield in the presence of an electron-withdrawing group due to the deshielding effect on the tellurium nucleus.

## Conclusions

The  $^{125}\text{Te}$  NMR chemical shift of organotellurium compounds is sensitive to the type and size of the substituents (aromatic, aliphatic) and the oxidation state of the Te atom. The chemical shift of the tellurides and telluronium salts moved *downfield* when an electron-withdrawing group was attached to the tellurium atom. On the other hand, the chemical shift of halooxatelluranes moved *upfield* when an electron-withdrawing group was attached. It will be important to consider the size and structure of the substituent as well as the electronic structure around the tellurium atom for the estimation of the chemical shift of organotellurium compounds. The results obtained in this study will be helpful in understanding the relationship between the structure and  $^{125}\text{Te}$  NMR chemical shift of organotellurium compounds.

## Experimental Section

**General Methods.** Common experimental procedures and instrumentation have been described previously.<sup>4</sup> Compounds **1-2**,<sup>4</sup> **3a**,<sup>5a</sup> and **4-6**<sup>5</sup> were prepared as reported. The procedure described in the preparation of **3a**<sup>5a</sup> was generally followed to prepare **3b** and **3c**.

**(R<sub>Te</sub>)-(-)-(4-[trifluoromethyl]phenyl){(1S,2R,4R)-2-hydroxy-7,7-**

**dimethylbicyclo[2.2.1]heptan-1-yl} methyl)telluronium chloride (3b):** colorless needles, mp 189–190 °C (recrystallized from EtOH);  $[\alpha]_{\text{D}}^{27}$  -11.25 ° (c 0.95, CHCl<sub>3</sub>); IR (KBr) 3139 (br), 2929, 1602, 1396, 1329, 1162, 1126, 1076, 1048, 1012, 820, 679 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.77 (s, 3H), 1.05 (s, 3H), 0.88–1.30 (m, 2H), 1.70–1.88 (m, 5H), 2.82 (s, 3H), 2.96 (d, *J* = 12.2 Hz, 1H), 3.27 (d, *J* = 12.5, 1H), 3.75 (m, 1H), 4.06 (dd, *J* = 3.8, 7.0, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (CD<sub>3</sub>OD) 23.9, 24.0, 32.1, 32.8, 39.5, 41.2, 47.4, 53.4, 58.6, 63.3, 90.7, 138.9 (q, *J*<sub>C-F</sub> = 272 Hz), 139.1 (q, *J*<sub>C-F</sub> = 3.7 Hz), 143.2, 145.8 (q, *J*<sub>C-F</sub> = 32.2 Hz); Anal. Calcd. for C<sub>18</sub>H<sub>24</sub>OF<sub>3</sub>ClTe: C, 45.38; H, 5.08. Found: C, 45.43; H, 4.93.

**(R<sub>Te</sub>)-(-)-(4-methoxyphenyl){(1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl} methyl)telluronium chloride (3c):** colorless needles, mp 133–135 °C (recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane);  $[\alpha]_{\text{D}}^{27}$  +20.09 ° (c 0.93, CHCl<sub>3</sub>); IR (KBr) 3252 (br), 2952, 1587, 1497, 1293, 1254, 1184, 1074, 1028, 825 cm<sup>-1</sup>; <sup>1</sup>H NMR δ: 0.72 (s, 3H), 1.05 (s, 3H), 0.82–1.29 (m, 2H), 1.62–1.88 (m, 5H), 2.78 (s, 3H), 3.02 (d, *J* = 12.5 Hz, 1H), 3.36 (d, *J* = 12.2 Hz, 1H), 3.72–3.86 (m, 1H), 3.84 (s, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 15.7, 21.3, 21.2, 27.2, 32.2, 35.0, 40.5, 45.6, 47.7, 50.7, 55.4, 77.2, 114.7, 115.8, 135.2, 161.9; Anal. Calcd. for C<sub>18</sub>H<sub>27</sub>ClO<sub>2</sub>Te: C, 49.31; H, 6.21. Found: C, 49.19; H, 6.20.

## Acknowledgment

This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

## References and Notes

- † Present address: Institute for Chemical Reaction Sciences, Tohoku University, Sendai, 980-8578, Japan. E-mail: ssaito@mail.cc.tohoku.ac.jp.
- ‡ Deceased, January 12, 1998.
- For review, see McFarlane, C. E., McFarlane, W. Sulfur, Selenium, and Tellurium. In: *Multinuclear NMR*. Mason I., Ed. Plenum Press: New York, 1987; pp 417–435.
  - (a) Zumbulyadis, N.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *192*, 183–188. (b) McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc. Dalton*, **1973**, 2416–2418. (c) Kohne, B.; Lohner, W.; Praefcke, K.; Jakobsen, H. J.; Villadsen, B. *J. Organomet. Chem.* **1979**, *166*, 373–377. (d) Gomblér, W. Z. *Naturforsch.* **1980**, *36B*, 535–543. (e) Denny, D. B.; Denny, D. Z.; Hammond, P. J.; Hsu, Y. F. *J. Am. Chem. Soc.* **1981**, *103*, 2340–2347. (f) Chadha, R. K.; Miller, J. M. *Can. J. Chem.* **1982**, *60*, 2256–2258. (g) Michalak, R. S.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7529–7539. (h) Jones, C. H. W.; Sharma, R. D.; Taneja, S. P. *Can. J. Chem.* **1986**, *64*, 980–986. (i) Detty, M. R.; Lenhart, W. C.; Gassman, P. G.; Callstrom, M. R. *Organometallics*, **1989**, *8*, 861–865. (j)

- Shimizu, T.; Urakubo, T.; Kamigata, N. *J. Org. Chem.* **1996**, *61*, 8032-8038. (k) Ruiz-Morales, Y.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem. A.* **1997**, *101*, 4121-4127.
3. Takahashi, T.; Zhang, J.; Kurose, N.; Takahashi, S.; Koizumi, T.; Shiro, M. *Tetrahedron: Asymmetry* **1996**, *7*, 2797-2800.
  4. Takahashi, S.; Zhang, J.; Saito, S.; Koizumi, T. *Heterocycles* **1997**, *46*, 373-384.
  5. (a) Zhang, J.; Saito, S.; Koizumi, T. *Tetrahedron: Asymmetry* **1997**, *8*, 3357-3361. (b) Zhang, J.; Saito, S.; Koizumi, T. *J. Org. Chem.* **1998**, *63*, 5423-5429.
  6. Dean, P. A. W.; Manivannan, V.; Vittal, J. J.; *Inorg. Chem.* **1989**, *28*, 2360-2368.
  7. On the other hand, no coupling between the fluorine atom and the selenium atom of a fluorooxaselenurane was observed (ref. 8). These results indicate that the rate of the halogen exchange reaction of a halooxaselenurane is much faster compared to that of a halooxatellurane.
  8. Saito, S.; Zhang, J.; Koizumi, T. *J. Org. Chem.* **1998**, *63*, 6029-6030
  9. A similar result has been reported for trichlorotelluranes (ref. 2f).
  10. This assumption is based on the result we obtained during the observation of  $^{77}\text{Se}$  NMR of highly ionic halooxaselenuranes (ref. 8).
  11. The electronegativity values were collected from Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific & Technical: Harlow, 1987; p. 31.
  12. We think that the resonance structures B and C have more important contribution than the resonance structures D and E, since a larger coupling constant between the Te atom and F atom was observed when an electron-donating group was attached to the benzene ring of the fluorooxatelluranes (Table 1, entries 4-6).