

Synthesis of Isolable Thiirane 1-Imides and Their Stereospecific Ring-enlargement to 1,2-Thiazetidines

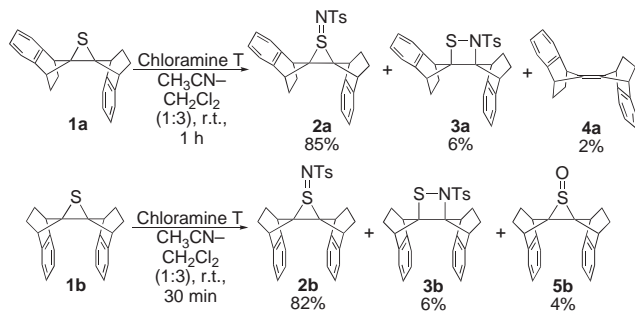
Yoshiaki Sugihara,* Yui Aoyama, Haruki Okada, and Juzo Nakayama*
 Department of Chemistry, Graduate School of Science and Engineering, Saitama University,
 Sakura-ku, Saitama 338-8570

(Received April 14, 2008; CL-080385; E-mail: ysugi@chem.saitama-u.ac.jp)

The isolation of thiirane 1-imides was achieved via imination of *anti*- and *syn*-9,9'-bibenzonorbornenylidene sulfides by Chloramine T at room temperature, followed by crystallization of the reaction mixture at -18°C . Allowing CD_2Cl_2 solutions of the thiirane 1-imides stand at room temperature or heating their crystals to around 120°C led to the formation of the corresponding 1,2-thiazetidines with retention of the configuration of the thiirane 1-imides.

In our continuing interest in the chemistry of *anti*- and *syn*-9,9'-bibenzonorbornenylidenes and their derivatives,¹ we reported that methylsulfonium salts of *anti*- and *syn*-9,9'-bibenzonorbornenylidene sulfides were synthesized by reactions of *anti*-sulfide **1a** and *syn*-sulfide **1b** with Me_3OBF_4 at low temperature and isomerized each other in CDCl_3 above room temperature.² In this connection, we have been greatly interested in chemistry of *S*-aminothiiranium salts and thiirane 1-imides. While a large number of studies of the chemistry of thiirane 1-oxides has been reported,³ only a few reports have dealt with thiirane 1-imides as a reaction intermediate.^{4,5} We report here the synthesis of the first isolable thiirane 1-imides by imination of thiiranes and their stereospecific ring-enlargement to 1,2-thiazetidines.

Chloramine T was used successfully as an imination agent for the synthesis of thiirane 1-imides (Scheme 1).⁶ Thus, the imination of **1a** in $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ (1:3) at room temperature followed by crystallization of the reaction mixture from CH_2Cl_2 -hexane at -18°C gave *anti*-thiirane 1-imide **2a** as colorless crystals in 85% yield. The resulting filtrate was purified by silica-gel column chromatography to afford *anti*-1,2-thiazetidine **3a**, the second isolable 1,2-thiazetidine,⁷ and **4a** in 6 and 2% yields, respectively. The same procedure for **1b** gave **2b**, **3b**, and **5b** in 82, 6, and 4% yields, respectively. The reaction mixture of **1a** was crystallized at room temperature to give **3a** in 62% yield; no trace amount of **2a** was observed. On the other hand, the imination of **1a** with $\text{PhI}=\text{NTs}$ in the presence of Cu^{I} catalyst did not provide **2a**.⁸

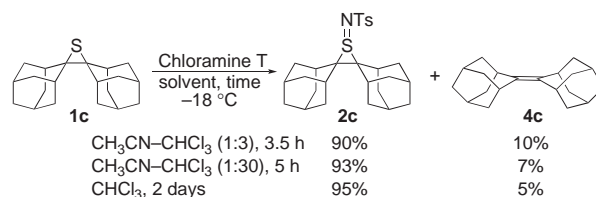


Scheme 1.

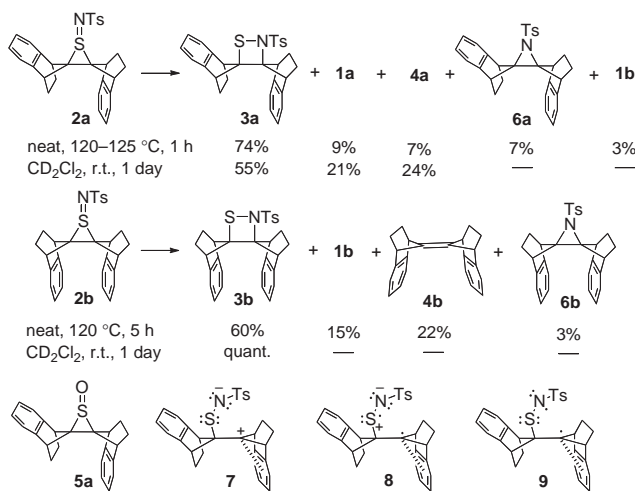
The imination of 2,2'-biadamantylidene sulfide **1c**⁹ in $\text{CH}_3\text{CN}-\text{CHCl}_3$ (1:3) at -18°C for 3.5 h gave **2c** and **4c** in 90 and 10% yields, respectively (Scheme 2). As the proportion of CH_3CN in the solvent was smaller, the yield of **2c** increased slightly but the reaction time was prolonged. *trans*-Stilbene sulfide **1d**, which carries two less hindered phenyl groups, reacted with Chloramine T at -18°C to give *trans*-stilbene **4d** in 95% yield stereoselectively, whereas *cis*-stilbene sulfide **1e** to form *cis*-stilbene **4e** in 60% yield together with **4d** in 28% yield. Steric crowding around the thiirane imide moiety probably stabilizes **2a-2c** kinetically.

The thiirane 1-imides, **2a** and **2b**, are thermally more labile than the corresponding thiirane 1-oxides, **5a** and **5b**. Thus, **2a** and **2b** were heated neat above 120°C to provide **3a** and **3b**, respectively, in which the stereochemistry of the thiirane 1-imide was retained (Scheme 3), while **5a** and **5b** melt without decomposition at $224-226$ and $211-212^{\circ}\text{C}$, respectively. Even letting CD_2Cl_2 solutions of **2a** and **2b** stand at room temperature also led to the stereospecific formation of **3a** and **3b**, respectively.

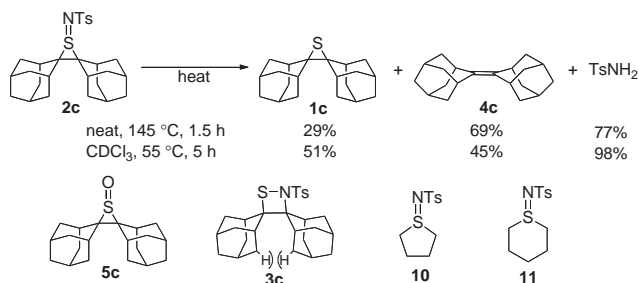
The probable mechanism of the formation of **3a** is as follows. The C-S bond that faces the ethylene bridge of **2a** is



Scheme 2.



Scheme 3.



cleaved to form intermediate **7** or **8**. The neighboring group participation of the benzene ring both assists to open the thiirane ring and stabilizes the intermediate. Recombination of the cation and anion centers in **7** or the two radical centers in **9** that is formed from **8** gives **3a**. This process is more rapid than rotation about the central C–C bond of **7** or **9**.

The thiirane 1-imide **2c** decomposed on heating both neat at 145 °C and in CDCl₃ at 55 °C to form **1c**, **4c**, and TsNH₂ (Scheme 4). The thermal decomposition would proceed as follows. Initially, **4c** and TsN=S^{4,10} are formed similar to the thermolysis of **5c** in refluxing toluene forming **4c** and intermediary S=O.¹¹ Water as an impurity or the resulting TsN=S attacks the nitrogen atom on **2c** to afford **1c** and TsN=S=X (X = NTs or O). Finally the remaining TsN=S and TsN=S=X were hydrolyzed to form TsNH₂ together with SO₂¹² and SO₂, respectively. Steric repulsion between the substituents in the transition state of the reaction of **2c** to **3c** is probably much more serious than those from **2a** and **2b**.

The ¹³C NMR spectra of **2** in CDCl₃ at –20 °C show eleven-sp³ and fifteen-sp² carbon peaks for **2a**,¹³ six-sp³ and ten-sp² carbon peaks for **2b**, and eleven-sp³ and four-sp² carbon peaks for **2c**. Thus, **2a** is not symmetric, and **2b** and **2c** have C_s symmetry in which the plane bisects the plane of the thiirane ring vertically through the S–N bond. Inversion of the pyramidal sulfur atom was not observed under these conditions. The ring carbon signals of the thiirane 1-imides (**2a**: δ 82.8, 83.7, **2b**: δ 79.9, **2c**: δ 77.3) appear at lower fields than do those of the corresponding thiiranes (**1a**: δ 74.7, 75.2, **1b**: δ 72.3, **1c**:^{11b} δ 71.7) and thiirane 1-oxides (**5a**: δ 80.6, 81.7, **5b**: δ 78.5, **5c**:^{11b} δ 72.9). Thus, the C–S bond electrons in the thiirane ring would be withdrawn more strongly by the *N*-tosylsulfilimine parts in **2** than by the sulfoxide parts in **5**. In the IR spectra, very strong S–N stretching absorption appeared at 970 for **2a**, 956 for **2b**, and 961 cm^{–1} for **2c**, respectively. These values are almost the same as are 965 for **10** and 966 cm^{–1} for **11**.¹⁴ The ring size of **2** slightly affects the value of the S–N stretch absorption.

The molecular structure of **3a** is shown in Figure 1.¹⁵ The 1,2-thiazetididine ring adopts a puckered structure with the

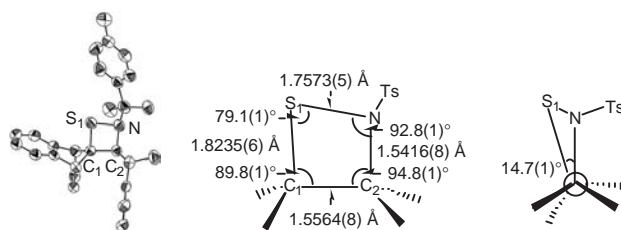


Figure 1. Molecular structure of **3a**.

S₁–C₁–C₂–N dihedral angle of 14.7(1)°, and the N₁ atom is pyramidal. The molecule of **3a** has no symmetry elements in the crystals. The C₂–N bond [1.5416(8) Å] is much longer than the common C–N bond (1.47 Å).¹⁶ Other bond lengths in the 1,2-thiazetididine ring are almost same as the common C–C (1.53 Å),¹⁶ C–S (1.82 Å),¹⁶ and S–N (1.76 Å)¹⁷ bond lengths.

The ¹³C NMR spectra of **3a** and **3b** in CDCl₃ at 25 °C appear that they both have seven-sp³ and ten-sp² carbon peaks in which the ring carbon signals appear at δ 84.5 and 94.2 for **3a** and δ 83.3 and 96.3 for **3b**, respectively. The 1,2-thiazetidines are symmetric under the conditions, so that both inversion of the pyramidal nitrogen atom and puckering of the nonplanar 1,2-thiazetididine ring take place.

References and Notes

- a) Y. Sugihara, K. Noda, J. Nakayama, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2351. b) Y. Sugihara, K. Noda, J. Nakayama, *Tetrahedron Lett.* **2000**, *41*, 8907. c) Y. Sugihara, K. Noda, J. Nakayama, *Tetrahedron Lett.* **2000**, *41*, 8911. d) K. Noda, Y. Sugihara, J. Nakayama, *Heteroat. Chem.* **2001**, *12*, 625.
- Y. Sugihara, Y. Aoyama, J. Nakayama, *Chem. Lett.* **2001**, 980.
- a) I. A. Abu-Yousef, D. N. Harpp, *J. Sulfur Chem.* **1997**, *20*, 1. b) D. C. Dittmer, in *Comprehensive Heterocyclic Chemistry*, ed. by A. R. Katritzky, C. W. Rees, Pergamon, Oxford, **1984**, Vol. 7, Chap. 5.06. c) W. Ando, N. Choi, N. Tokitoh, in *Comprehensive Heterocyclic Chemistry II*, ed. by A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Pergamon, Oxford, **1996**, Vol. 1, Chap. 1.05.
- P. Reynolds, S. Zonnebelt, S. Bakker, R. M. Kellogg, *J. Am. Chem. Soc.* **1974**, *96*, 3146.
- Y. Hata, M. Watanabe, *J. Org. Chem.* **1980**, *45*, 1691.
- a) A. L. Marzinzik, K. B. Sharpless, *J. Org. Chem.* **2001**, *66*, 594. b) F. Ruff, A. Kucsman, *J. Chem. Soc., Perkin Trans. 2* **1982**, 1075. c) F. G. Mann, W. J. Pope, *J. Chem. Soc., Trans.* **1922**, *121*, 1052.
- The first isolable 1,2-thiazetididine: T. Otani, J. Takayama, Y. Sugihara, A. Ishii, J. Nakayama, *J. Am. Chem. Soc.* **2003**, *125*, 8255.
- a) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, C. P. Baird, T. J. Sparey, P. C. Taylor, *J. Org. Chem.* **1997**, *62*, 6512. b) T. Otani, Y. Sugihara, A. Ishii, J. Nakayama, *Tetrahedron Lett.* **1999**, *40*, 5549.
- J. Nakayama, Y. Ito, A. Mizumura, *Sulfur Lett.* **1992**, *14*, 247.
- O. Meth-Cohn, G. Vuuren, *J. Chem. Soc., Perkin Trans. 1* **1986**, 245.
- a) I. A. Abu-Yousef, D. N. Harpp, *Tetrahedron Lett.* **1995**, *36*, 201. b) I. A. Abu-Yousef, D. N. Harpp, *J. Org. Chem.* **1997**, *62*, 8366.
- J. Nakayama, Y. Tajima, P. Xue-hua, Y. Sugihara, *J. Am. Chem. Soc.* **2007**, *129*, 7250.
- One of the fifteen-sp² carbon peaks is due to a degeneracy of two carbon peaks.
- K. Tsujihara, N. Furukawa, S. Oae, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2153.
- Crystal data for **3a**: triclinic, P $\bar{1}$, *a* = 10.576(1), *b* = 10.843(1), *c* = 11.779(1) Å, α = 68.253(3), β = 73.390(2), γ = 78.866(4)°, *V* = 1196.50(10) Å³, *Z* = 2, *D*_{calcd} = 1.348 Mg m^{–3}, *R* = 0.053, *wR* = 0.070, *S* = 1.166.
- E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley-Interscience, New York, **1994**, p. 13.
- S. Oae, N. Furukawa, *Sulfilimines and Related Derivatives*, American Chemical Society, Washington, D. C., **1983**, p. 53.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/>.