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

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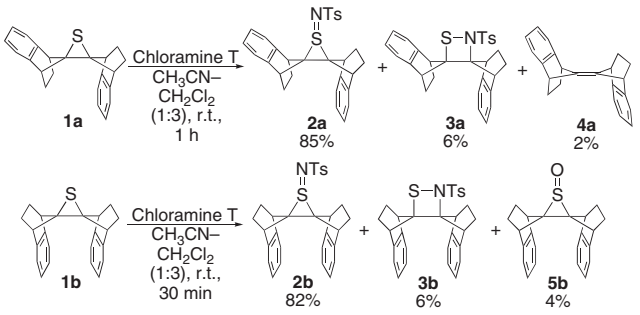
The isolation of thiirane 1-imides was achieved via imination of *anti*- and *syn*-9,9′-bibenzonorbornenylidene sulfides by Chloramine T at room temperature, followed by crystallization of the reaction mixture at −18 °C. Allowing CD_2Cl_2 solutions of the thiirane 1-imides stand at room temperature or 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 CH_3CN–CH_2Cl_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 PhI=NTs in the presence of Cu^I catalyst did not provide **2a**.[8]

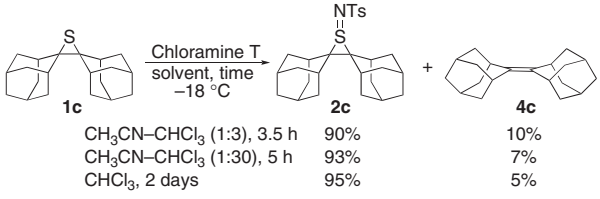


Scheme 1.

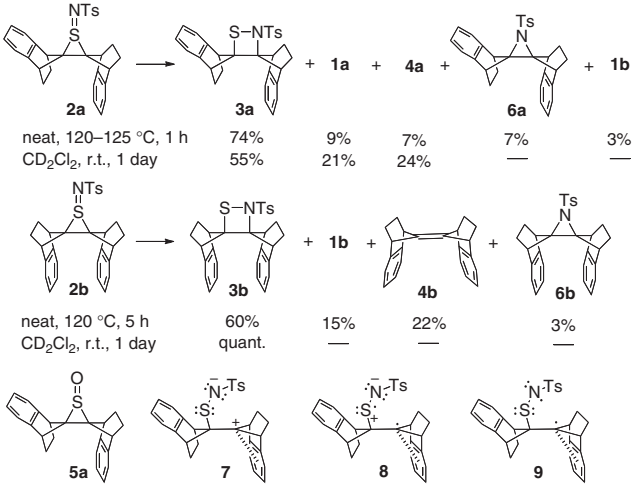
The imination of 2,2′-biadamantylidene sulfide **1c**[9] in CH_3CN–$CHCl_3$ (1:3) at −18 °C for 3.5 h gave **2c** and **4c** in 90 and 10% yields, respectively (Scheme 2). As the proportion of CH_3CN in the solvent was smaller, the yield of **2c** increased slightly but the reaction time was prolonged. *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 crowdness 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 °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.

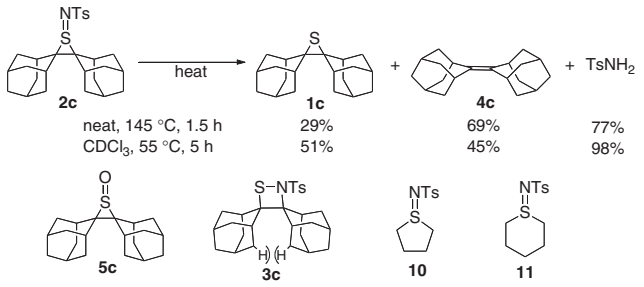
The probable mechanism of the formation of **3a** is as follows. The C–S bond that faces the ethylene bridge of **2a** is



Scheme 2.



Scheme 3.



Scheme 4.

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 $CDCl_3$ at 55 °C to form **1c**, **4c**, and $TsNH_2$ (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 $TsNH_2$ together with SO[12] and SO_2, 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 ^{13}C NMR spectra of **2** in $CDCl_3$ at −20 °C show eleven-sp^3 and fifteen-sp^2 carbon peaks for **2a**,[13] six-sp^3 and ten-sp^2 carbon peaks for **2b**, and eleven-sp^3 and four-sp^2 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-thiazetidine ring adopts a puckered structure with the S_1–C_1–C_2–N dihedral angle of 14.7(1)°, and the N_1 atom is pyramidal. The molecule of **3a** has no symmetry elements in the crystals. The C_2–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-thiazetidine 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.

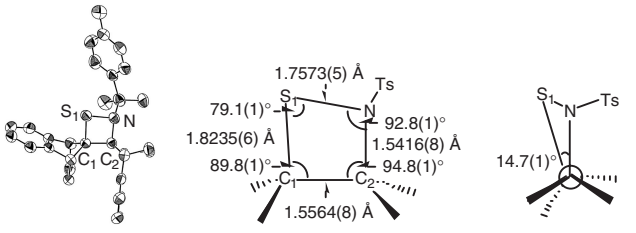


Figure 1. Molecular structure of **3a**.

The ^{13}C NMR spectra of **3a** and **3b** in $CDCl_3$ at 25 °C appear that they both have seven-sp^3 and ten-sp^2 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-thiazetidine ring take place.

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15 Crystal data for **3a**: triclinic, $P\bar{1}$, $a = 10.576(1)$, $b = 10.843(1)$, $c = 11.779(1)$ Å, $\alpha = 68.253(3)$, $\beta = 73.390(2)$, $\gamma = 78.866(4)$°, $V = 1196.50(10)$ Å^3, $Z = 2$, $D_{calcd} = 1.348$ Mg m^{-3}, $R = 0.053$, $wR = 0.070$, $S = 1.166$.

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