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Journal of Organometallic Chemistry 611 (2000) 172–177

Journal of Organometallic Chemistry

Desulfurilative self-coupling reaction of 1,3-thiazolidine-2-thiones and intramolecular non-bonded S···S interaction in the crystallographic structure of the products

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Received 30 March 2000; accepted 18 April 2000

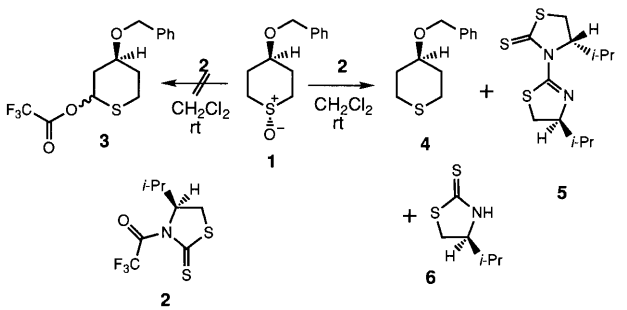
Abstract

An attempt at an asymmetric Pummerer-type reaction of *trans*-4-benzyloxythiane-1-oxide (**1**) with 3-trifluoroacetyl-4*S*-isopropyl-1,3-thiazolidine-2-thione (**2**) resulted in failure but an attractive desulfurilative self-coupling reaction of 4*S*-isopropyl-1,3-thiazolidine-2-thione (**6**) occurred to give 4*S*-isopropyl-3-(4*S*-isopropyl-1,3-thiazolin-2-yl)-1,3-thiazolidine-2-thione (**5**). The same desulfurilative self-coupling reaction of compound **6** or **11** efficiently proceeded by treatment of diphenyl sulfoxide (**7a**) or methyl phenyl sulfoxide (**7b**) with **2** or 3-trifluoroacetyl-1,3-thiazolidine-2-thione (**8**) to afford each corresponding product **5** or **9**. Eventually, we found a practically useful method for the synthesis of **5** and **9** by exploiting $TiCl_4$ and sodium salt **12** or **13** of 1,3-thiazolidine-2-thiones. Interestingly, intramolecular non-bonded S···S interactions were recognized in the crystallographic structures of **5** and **9**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Pummerer-type reaction; Sulfoxide; 4*S*-Isopropyl-1,3-thiazolidine-2-thione; 1,3-Thiazolidine-2-thione; Coupling reactions; Non-bonded interactions; X-ray crystallographic analysis

1. Introduction

Intramolecular non-bonded S···X (X = O, S, N, etc.) interactions have been investigated for characterization of the molecular structures of a large number of organosulfur compounds [1]. These intra- and intermolecular non-bonded interactions seem to be very attractive from a viewpoint of the construction of a new molecular recognition system in chemical reactions [2] and medicinal biochemistry [3]. In the series of studies on heterocycles such as thiazolidines, thiazoles, thiadiazoles, and their related compounds, we have developed various asymmetric induction reactions employing C4-chiral 1,3-thiazolidine-2-thiones [4] and clarified intramolecular non-bonded 1,5-type S···O interactions in 2-acylamino-1,3,4-thiadiazoles and 2-acylimino-1,3,4-thiadiazolines as angiotensin II receptor antagonists [5]. Recently, we attempted an asymmetric Pummerer-type reaction of *trans*-4-benzyloxythiane-1-oxide (**1**), adopting a preferential *trans*-diaxial conformer [6], with 3-trifluoroacetyl-4*S*-isopropyl-1,3-thiazolidine-2-thione (**2**) in CH_2Cl_2 at room temperature, as shown in Scheme 1. However, the desirable reaction to give **3** did not occur, and the resultant reaction furnished 4*S*-



Scheme 1.

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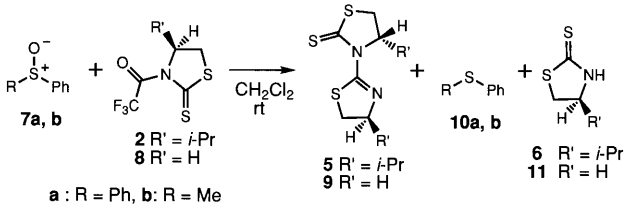
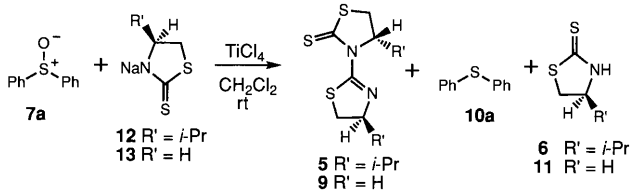
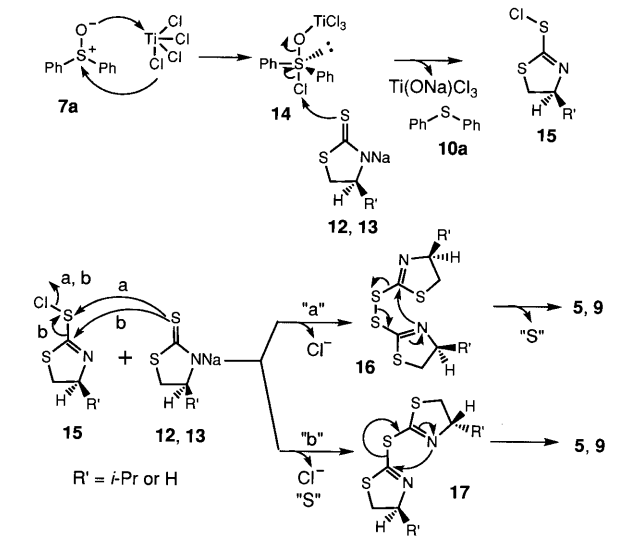
PII: S0022-328X(00)00460-5



Scheme 2.



Scheme 3.



Scheme 4.

isopropyl-3-(4*S*-isopropyl-1,3-thiazolin-2-yl)-1,3-thiazolidine-2-thione (**5**) in 46% yield, 4-benzyloxythiane (**4**) in 69% yield, and a trace amount of 4*S*-isopropyl-1,3-thiazolidine-2-thione (**6**). The chiral bicyclic heterocycle **5** seemed to be a new chiral ligand molecule for some soft-acidic Lewis acids. Thus, we wished to research more practically useful reaction conditions in order to obtain the chiral heterocycle **5**.

2. Result and discussion

2.1. Synthesis of bicyclic heterocycles 5 and 9

First of all, we examined a Pummerer-type reaction by using commercially available diphenyl sulfoxide (**7a**) and methyl phenyl sulfoxide (**7b**) instead of **1**. Treatment of **7a** or **7b** with 3-trifluoroacetyl-1,3-thiazolidine-2-thione (**8**) in CH_2Cl_2 at room temperature gave 3-(1,3-thiazolin-2-yl)-1,3-thiazolidine-2-thione (**9**) (45% or 35% yield), diphenyl sulfide (**10a**) (59% yield) or thioanisole (**10b**) (40% yield), and a trace amount of 1,3-thiazolidine-2-thione (**11**), respectively, as shown in Scheme 2. The structure of **9** was confirmed to be that of the known compound [7], obtained from totally different synthetic methods from the present procedure, on the basis of the physical and spectroscopic data. Subsequently, the same treatment of **7a** or **7b** with 3 - trifluoroacethyl - 4*S* - isopropyl - 1,3 - thiazolidine - 2-thione (**2**) as described above afforded 4*S*-isopropyl-3-(4*S* - isopropyl - 1,3 - thiazolin - 2 - yl) - 1,3 - thiazolidine - 2-thione (**5**) (45% or 35% yield) together with each corresponding sulfide **10a** (59% yield) or **10b** (40% yield) and **6**.

The structure of the new chiral heterocyclic compound **5** was determined by X-ray crystallographic analysis (vide infra). Because 3-trifluoroacetyl-1,3-thiazolidine-2-thiones (**2** and **8**) were remarkably unstable, an alternative synthetic method for **5** and **9** was investigated by using a Lewis acid as follows. Diphenyl sulfoxide (**7a**) was tentatively treated with sodium salt **12** [8] or **13** of 1,3-thiazolidine-2-thiones in the presence of $TiCl_4$ in CH_2Cl_2 at room temperature, as shown in Scheme 3. The desired reaction proceeded smoothly to give **5** in 46% yield or **9** in 53% yield and diphenyl sulfide (**10a**) in 65% or 59% yield, respectively. This practically useful reaction for the synthesis of **5** and **9** using $TiCl_4$ and diphenyl sulfoxide (**7a**) can be explained by speculative reaction mechanisms, as shown in Scheme 4. Namely, the reaction of **7a** with $TiCl_4$ presumably generates a sulfurane intermediate **14** [9], followed by nucleophilic attack by **12** or **13** to furnish sulfenyl chloride **15** and diphenylsulfide (**10a**). The resultant labile **15** may immediately react with **12** or **13** in two ways, 'a' and 'b', giving disulfide **16** and/or sulfide **17** releasing Cl^- or Cl^- and sulfur atom. Both unstable intermediates **16** and **17** would become stable compound **5** or **9** via intramolecular nucleophilic reaction releasing sulfur atom or via S → N rearrangement reaction [10], respectively. In the reaction (Scheme 2) with 3-trifluoroacetyl-1,3-thiazolidine-2-thiones (**2** and **8**), the reaction mechanism probably involves the formation of a sulfurane intermediate **18**, followed by nucleophilic attack by the corresponding 1,3-thiazolidine-2-thione anions to give **16** and/or **17**, as shown in Fig. 1.

2.2. Characterization of the crystallographic structures of 5 and 9

In order to clarify the structure of **5**, the crystalline compound **5** was submitted to X-ray crystallographic

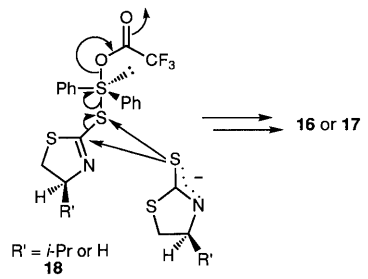


Fig. 1. Speculative reaction mechanism for the reaction of Scheme 2.

Table 1
Summary of X-ray crystallographic analyses of compounds **5** and **9**

	5	**9**
Formula	$C_{12}H_{20}N_2S_3$	$C_6H_8N_2S_3$
Formula weight	288.48	204.32
Crystal description	Yellow prism	Yellow prism
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
Lattice parameters		
a (Å)	11.858(2)	7.766(3)
b (Å)	5.873(2)	12.742(5)
c (Å)	12.516(2)	17.90(1)
β (°)	116.85(1)	98.79(4)
Volume (Å^3)	777.6(3)	1749.9900
Z	2	8
Density (calculated) (g cm^{-3})	1.232	1.551
Residual R, R_w	0.058, 0.074	0.057, 0.073
Goodness-of-fit	1.48	1.83
p-factor	0.0820	0.0610

analysis (Tables 1 and 2). The computer-generated drawing of the crystal structure of **5** proved to be the desired desulfurilative bicyclic product, as shown in Fig. 2. In the represented crystalline structure of **5**, significant close contact [3.039(3) Å] between S2 and S3 atoms and planarity of the S2–C3–N1–C7–S3 moiety were recognized (see torsion angles in Table 2.). Subsequently, X-ray crystallographic analysis of **9** was carried out (Tables 1 and 2). Similar close contact [3.024(2) or 3.028(2) Å] between S2 and S3 or between S5 and S6 in both crystalline structures (**A** and **B**) of **9** was also recognized. The S2–C3–N1–C4–S3 and S5–C9–N3–C10–S6 moieties in the structures **A** and **B** are almost flat from the viewpoint of the related torsion angles listed in Table 2. In the molecules **5** and **9**, the non-bonded S···S atoms distances are considerably shorter than the sum (3.60 Å) of the van der Waals radii (S and S). There have been several papers that have discussed the non-bonded S···S interaction, e.g. in geometrically constrained 1,5-dithiocane derivatives [11], 1-tosylimino-1,5-dithiacyclooctane [12], bis(phenylthio)-dibenzothiophenes [13], thiathiophthenes ('bond switching') [1e,g] etc.[14]. The 1,5-type intramolecular non-bonded S···S interaction in the bicyclic heterocycles **5** and **9** may be regarded as another new type of close contact and compound **9** will be a useful chiral ligand for soft Lewis acids.

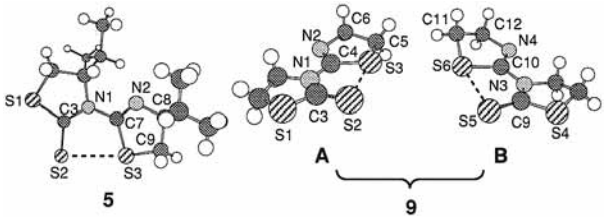


Fig. 2. Computer-generated drawing derived from the X-ray coordinates of compounds **5** and **9**.

3. Experimental

3.1. General methods

All melting points were determined on a Yanagimoto microapparatus and are uncorrected. The infrared (IR)

Table 2
Selected atom distances (Å), bond angles (°), and torsion angles (°) in the structures **5** and **9** (**A** and **B**)

5		**9** (**A**)		**9** (**B**)	
S2–S3	3.039(3)	S2–S3	3.024(2)	S5–S6	3.028(2)
	3.60 [a]		3.60 [a]		3.60 [a]
C3–N1	1.364(7)	C3–N1	1.362(4)	C9–N3	1.369(5)
N1–C7	1.409(8)	N1–C4	1.405(5)	N3–C10	1.411(5)
C3–S2	1.648(7)	C3–S2	1.645(5)	C9–S5	1.639(5)
S3–C7–N1	122.2(5)	S3–C4–N1	122.6(3)	S6–C10–N3	122.9(3)
C7–N1–C3	127.3(5)	C4–N1–C3	126.7(4)	C10–N3–C9	126.1(4)
N1–C3–S2	128.5(5)	N1–C3–S2	129.2(3)	N3–C9–S5	129.2(4)
C7–S3–C9	87.8(4)	C4–S3–C5	88.9(2)	C10–S6–C11	87.7(2)
S3–C7–N1–C3	5.6(10)	S3–C4–N1–C3	4.5(6)	S6–C10–N3–C9	6.9(6)
S2–C3–N1–C7	−13.0(10)	S2–C3–N1–C4	−3.9(6)	S5–C9–N3–C10	1.1(6)

[a] Sum of van der Waals radii (S and S).

spectra were recorded on a Perkin–Elmer 1720 IR Fourier transform spectrometer. ^{1}H-NMR (200 and 300 MHz) and ^{13}C-NMR spectra were recorded on a JEOL-FX200 or JEOL-AL300 spectrometer. Chemical shifts are given in δ values (ppm) using tetramethylsilane as an internal standard. Electron impact (EI) mass spectra [MS and high resolution (HR)] were obtained on a JEOL-SX-102A instrument. Elementary combustion analyses were performed by Yanagimoto CHN corder and are within 0.4% of theoretical values. Optical rotations were recorded on a JASCO DIP-370 polarimeter. All reactions were monitored by thin-layer chromatography employing 0.25 mm E. Merck silica gel plates (60F-254). Preparative thin-layer chromatography was performed on 0.5 mm E. Merck silica gel plates (60F-254). Column chromatography was carried out on E. Merck silica gel (60-9385, 230-400 mesh) or Katayama silica gel (60-K070, 70-230 mesh). Usual workup means washing with a water solution saturated with NaCl, drying the organic portion over $MgSO_4$, filtration, and evaporation in vacuo.

3.2. Synthesis and reaction of *trans*-4-benzyloxythiane-1-oxide (**1**)

3.2.1. Synthesis of 4-benzyloxythiane (**4**)

To a solution of tetrahydrothiopyran-4-ol (500 mg, 4.23 mmol) in THF (10 ml) was added 60% NaH (338 mg, 8.45 mmol) under Ar atmosphere at 0°C. The mixture was stirred at room temperature for 1 h and then at 40°C for 2 h. After addition of benzyl bromide (0.6 ml, 5.08 mmol) under ice-cooling, the mixture was stirred at 40°C for 4.5 h and then treated with 5% HCl. The acidic reaction mixture was extracted with AcOEt. The extract was submitted to the usual workup to give an oily residue, which was purified by silica gel column chromatography with hexane–AcOEt (20:1) to afford the pure product **4** (700 mg, 80% yield) as a colorless oil. IR (neat) 3030, 2934, 1390, 1266, 1034 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.78–1.95 (m, 2H), 2.07–2.21 (m, 2H), 2.44–2.57 (m, 2H), 2.79–2.91 (m, 2H), 3.38–3.49 (m, 1H), 4.54 (s, 2H), 7.33 (s, 5H). HREI-MS calc. for $C_{12}H_{16}OS$ MW 208.0922, found m/z 208.0912 (M +). Anal. Calc. for $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 69.39; H, 7.67%.

3.2.2. Synthesis of *trans*-4-benzyloxythiane-1-oxide (**1**)

To a solution of compound **4** in CH_2Cl_2 (50 ml) was added *m*-chloroperbenzoic acid (8.7 g, 50.4 mmol) at −78°C under N_2 atmosphere. After being stirred at −78°C for 3 h, the reaction mixture was filtered through a celite bed. The filtrate was submitted to the usual workup to obtain an oily residue. Purification o f the residue was done by silica gel column chromatography with $CHCl_3$–MeOH (50:1) to give a mixture of *trans*- and *cis*-4-benzyloxythiane-1-oxide as colorless crystals. Recrystallization of the mixture from hexane and AcOEt gave the *trans* product **1** (2.1 g, 40%) as colorless needles; m.p. 42°C. IR (neat) 2926, 1757, 1455, 1349, 1029, 913, 741, 701 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.93 (dd, 2H, J = 10.4, 4.5 Hz), 2.44–2.54 (m, 2H), 2.74 (bd, 2H, J = 13.4 Hz), 2.92 (td, 2H, J = 13.4, 3.5 Hz), 3.75 (m, 1H), 4.54 (s, 2H), 7.29–7.39 (m, 5H). HREI-MS calc. for $C_{12}H_{16}O_2S$ MW 224.0871, found m/z 224.0879 (M +). Anal. Calc. for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19. Found: C, 63.93; H, 7.11%.

3.2.3. Reaction of *trans*-4-benzyloxythiane-1-oxide (**1**) with compound **2**

To a solution of 4*S*-isopropyl-1,3-thiazolidine-2-thione (**6**) (105 mg, 0.65 mmol) in CH_2Cl_2 (2 ml) was added trifluoroacetic anhydride (900 μl, 6.30 mmol) at −10 to −15°C under Ar atmosphere. After being stirred at −10 to −15°C for 2 h, the reaction mixture was evaporated in vacuo to give a yellow crude product **2**. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.03 (d, 3H, J = 6.8 Hz), 1.08 (d, 3H, J = 6.8 Hz), 2.32–2.43 (m, 1H), 3.26 (dd, 1H, J = 2.4, 11.6 Hz), 3.36 (dd, 1H, J = 7.0, 11.6 Hz), 4.72–4.77 (m, 1H). HREI-MS calc. for $C_8H_{10}ONS_2F_3$ MW 257.0156, found m/z 257.0138 (M +). The crude **2** was dissolved in CH_2Cl_2 (4 ml) and then a solution of compound **1** (50 mg, 0.22 mmol) in CH_2Cl_2 (2 ml) was added at −10°C. After being stirred at room temperature for 20 h, the reaction mixture was treated with water and then extracted with CH_2Cl_2. The extract was submitted to the usual workup to give a yellow oily residue, which was chromatographed on a silica gel column with CH_2Cl_2–hexane (2:1) to afford 4*S*-isopropyl-3-(4*S*-isopropyl-1,3-thiazolin-2-yl)-1,3-thiazolidine-2-thione (**5**) (23 mg, 46%), 4-benzyloxythiane (**4**) (32 mg, 69%), and a trace amount of 4*S*-isopropyl-1,3-thiazolidine-2-thione (**6**). Compound **5**: yellow prisms; mp 98–100°C (hexane). IR (KBr) 2960, 1589, 1390, 1 266, 1034 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.94–1.06 (m, 12H), 1.79–1.89 (m, 1H), 2.57–2.66 (m, 1H), 2.92 (t, 1H, J = 11.0 Hz), 3.09 (d, 1H, J = 11.0 Hz), 3.26 (dd, 1H, J = 8.0, 10.5 Hz), 3.60 (dd, 1H, J = 8.8, 11.2 Hz), 3.81–3.94 (m, 1H), 5.20–5.27 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 198.7 (C=S), 155.8 (C=N). $[\alpha]_D^{13}$ + 108.0 (c 1.25, $CHCl_3$). HREI-MS calc. for $C_{12}H_{20}N_2S_3$ MW 288.0789, found m/z 288.0800 (M +). Anal. Calc. for $C_{12}H_{20}N_2S_3$: C, 49.96 ; H, 6.99; N, 9.71. Found: C, 49.98; H, 6.95; N, 9.55%.

3.3. Reaction of diphenyl sulfoxide (**7a**) or methyl phenyl sulfoxide (**7b**) with 3-trifluoroacetyl-1,3-thiazolidine-2-thiones (**2** and **8**)

3.3.1. Reaction of diphenyl sulfoxide (**7a**) with compound **2**

To a solution of 4*S*-isopropyl-1,3-thiazolidine-2-thione (**6**) (564 mg, 14.2 mmol) in CH_2Cl_2 (2 ml) was added trifluoroacetic anhydride (2 ml, 14.2 mmol) at

−10 to −15°C under Ar atmosphere. After being stirred at −10 to −15°C for 2 h, the reaction mixture was evaporated in vacuo to give a yellow crude product **2**. To a solution of crude **2** in CH_2Cl_2 (9 ml) was added a solution of diphenyl sulfoxide (**7a**) (354 mg, 1.75 mmol) at −10°C, and the mixture was stirred at room temperature for 26 h. After addition of water, the reaction mixture was extracted with CH_2Cl_2 and then the extract was submitted to the usual workup. The resultant yellow oily residue was chromatographed on silica gel plates with CH_2Cl_2–MeOH (50:1) to afford 4*S*-isopropyl-3-(4*S*-isopropyl-1,3-thiazolin-2-yl)-1,3-thiazolidine-2-thione (**5**) (157 mg, 45%), diphenyl sulfide (**10a**) (35 mg, 59%), and a trace amount of **6**.

3.3.2. Reaction of methyl phenyl sulfoxide (*7b*) with compound *2*

Similar treatment of **7b** (70 mg, 0.50 mmol) with crude **2**, obtained from the reaction of **6** (70 mg, 0.50 mmol) with trifluoroacetic anhydride (381 μl, 2.70 mmol) in CH_2Cl_2, gave compound **5** (102 mg, 35%), methyl phenyl sulfide (**10b**) (51 mg, 40%), and a trace amount of **6**.

3.3.3. Reaction of diphenyl sulfoxide (*7a*) with 3-trifluoroacetyl-1,3-thiazolidine-2-thione (*2*)

To a solution of 1,3-thiazolidine-2-thione (**11**) (81 mg, 0.66 mmol) in CH_2Cl_2 (2 ml) was added trifluoroacetic anhydride (268 μl, 1.9 mmol) at −10 to −15°C under Ar atmosphere. After being stirred at −10 to −15°C for 2 h, the reaction mixture was evaporated in vacuo to give a crude yellow product **8**. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.48 (t, 3H, $J = 7.1$ Hz), 4.56 (t, 3H, $J = 7.1$ Hz). HREI-MS calc. for $C_5H_4ONS_2F_3$ MW 214.9686, found m/z 214.9701 (M+). The crude product **8** was dissolved in CH_2Cl_2 (4 ml) and then a solution of diphenyl sulfoxide (**7a**) (67 mg, 0.33 mmol) in CH_2Cl_2 (2 ml) was added at −10°C. After being stirred at room temperature for 18 h, the reaction mixture was treated with water (10 ml) and then extracted with CH_2Cl_2. The extract was submitted to the usual workup to give a yellow oily residue, which was chromatographed on silica gel plates with CH_2Cl_2–MeOH (50:1) to afford 3-(1,3-thiazolidin-2-yl)-1,3-thiazolidine-2-thione (**9**) (23 mg, 45%), diphenyl sulfide (**10a**) (35 mg, 59%), and a trace amount of 1,3-thiazolidine-2-thione (**11**). All spectroscopic data of the synthesized compound **9** (yellow prisms, m.p. 79–80°C (CH_2Cl_2–hexane)) were identical with those of literature data [7].

3.3.4. Reaction of methyl phenyl sulfoxide (*7b*) with compound *8*

Similar treatment of **7b** (143 mg, 1.02 mmol) with crude **8**, obtained from the reaction of **11** (243 mg, 2.04 mmol) with trifluoroacetic anhydride (850 μl, 6.00 mmol) in CH_2Cl_2, gave compound **9** (32 mg, 35%), methyl sulfide (**10b**) (69 mg, 40%), and a trace amount of **11**, respectively.

3.3.5. Reaction of diphenyl sulfoxide (*7a*) with $TiCl_4$ in the presence of sodium salt *12* of 4S-isopropyl-1,3-thiazolidine-2-thione

To a solution of diphenyl sulfoxide (**7a**) (681 mg, 3.37 mmol) in CH_2Cl_2 (25 ml) was added $TiCl_4$ (450 μl, 4.10 mmol) at 0°C under Ar atmosphere, and the mixture was stirred at 0°C for 30 min. After addition of the sodium salt **12** (1.40 mg, 7.64 mmol) obtained by treatment of 4*S*-isopropyl-1,3-thiazolidine-2-thione (**6**) with 60% NaH in THF, the mixture was stirred at room temperature for 7 h and then treated with water. The aqueous solution was extracted with CH_2Cl_2, and the extract was submitted to the usual workup to give a yellow oily residue. The residue was chromatographed on a silica gel column with hexane–AcOEt (3:1) to afford 4*S*-isopropyl-3-(4*S*-isopropyl-1,3-thiazolin-2-yl)-1,3-thiazolidine-2-thione (**5**) (501 mg, 46%), diphenyl sulfide (**10a**) (389 mg, 65%), and a trace amount of **6**.

3.3.6. Reaction of diphenyl sulfoxide (*7a*) with $TiCl_4$ in the presence of sodium salt *13* of 1,3-thiazolidine-2-thione

Similar treatment of diphenyl sulfoxide (**7a**) (112 mg, 0.55 mmol) with $TiCl_4$ (73 μl, 0.66 mmol) and **13** (170 mg, 1.2 mmol) in CH_2Cl_2 gave 3-(1,3-thiazolin-2-yl)-1,3-thiazolidine-2-thione (**9**) (65 mg, 53%), diphenyl sulfoxide (**10a**) (60 mg, 59%), and a trace amount of **11**, respectively.

3.4. X-ray crystallographic analysis of compound *5*

The single crystals were obtained by recrystallization from hexane. All measurements were made on a Rigaku AFC7R diffractometer with filtered Cu–K_α radiation and a rotating anode generator. The data were corrected using the ω–2θ scan technique to a maximum 2θ value of 129.9°. A total of 1520 reflections was collected. A correction for secondary extinction was applied (coefficient 9.41120×10^{-7}). The structure was solved by direct methods [15] and expanded using Fourier techniques [16]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2013 observed reflections ($I > 3.00\sigma(I)$) and 200 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 0. 37 and −0.42 e Å^{-3}, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985 and 1999). The crystal data and the selected atom distances, bond angles, and torsion angles are listed in Tables 1 and 2, respectively.

3.5. X-ray crystallographic analysis of compound **9**

The single crystals were obtained by recrystallization from hexane–CH_2Cl_2. All measurements were made on a Rigaku RAXIS-IV imaging plate diffractometer with graphite monochromated Mo–K_α radiation. The data were corrected using an ω–2θ scan technique to a maximum 2θ value of 55.0°. A total of 2680 reflections was collected. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient 9.41120×10^{-7}). The structure was solved by direct methods [15] and expanded using Fourier techniques [16]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2013 observed reflections ($I > 3.00\sigma(I)$) and 200 variable parameters. The maximum and minimum peak on the final difference Fourier map corresponded to 0.37 and -0.42 e Å^{-3}, respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation (1985 and 1999). The crystal data and the selected atom distances, bond angles, and torsion angles are listed in Tables 1 and 2, respectively.

4. Supplementary material

Complete details have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 143786 for compound **5** and CCDC no. 143787 for compound **9**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was partly supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 11120239) from the Ministry of Education, Science, Sports, and Culture, Japan.

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