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Thiiranation of 2′-Adamantylidene-9-Benzonorbornenylidene Using 4,4′-Oligothiodimorpholine and Brønsted Acid

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ABSTRACT: *On leaving 4,4′-dithiodimorpholine* **6** *powder undisturbed at room temperature over 10 years, it led to the formation of 4,4′-tetrathiodimorpholine* **7**. *Reactions of 2′-adamantylidene-9-benzonorbornenyidene* **1** *with* **6**, **7**, *and 4,4′-thiodimorpholine* **8** *and a Brønsted acid in CH_2Cl_2 at room temperature proceeded to afford the corresponding thiiranes,* **2** *and* **3**. *The order of reactivity of 4,4′-oligothiodimorpholines combined with a Brønsted acid is* **7** > **6** > **8**. *The thiirane* **3** *was transformed to* **1** *and* **2** *under the reaction conditions.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:12–18, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20505

INTRODUCTION

The chemistry of three-membered heterocyclic compounds has been attracting considerable interest from the viewpoints of synthesis, structure, reactions, and synthetic applications [1–5]. Oxiranes and aziridines can easily be synthesized from alkenes by oxiranation (epoxidation) with an oxidant such as peracid and peroxide and by aziridination with a nitrene equivalent, respectively, and have been used as precursors for syntheses of functional materials and biologically active compounds [1–3]. Thiiranes are considered to be superior precursors to oxiranes and aziridines because their sulfur atom makes their conversion to other compounds more facile than that of oxiranes and aziridines having oxygen and nitrogen atoms, respectively [6–9]. Although syntheses of thiiranes have been investigated so far [4,5], fewer reports have dealt with thiiranation of alkenes in comparison with the oxiranation and aziridination [10]. There are problems with the thiiranation, such as being limited to alkenes used, difficulty of synthesizing a sulfuration reagent, and further reactions of the resulting thiirane. One of the most widely used laboratory methods for thiirane synthesis has been a two-step transformation of alkenes to thiiranes through oxiranes.

We have studied the chemistry of sterically hindered alkenes such as 9,9′-bibenzonorbornenylidenes, 2′-adamantylidene-9-benzonorbornenylidene **1**, and related compounds [11–17]. In the course of that study, we found that **1** reacted with sulfuration reagents to afford the corresponding thiiranes **2** and **3** [17]. Thus, heating **1** with elemental sulfur in o-$Cl_2C_6H_4$ or *N*,*N*-dimethylformamide (DMF) gave an approximately 16:1 or 9:1 mixture of **2** and **3** together with **1**. The alkene **1** reacted with S_XCl_2 ($X = 1$, 2) at −78°C to

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give **2** and *vic*-dichloride **4**. No other products were observed in the reactions. The thiirane **3** isomerized easily to **2**, which is thermally more stable than **3** by 3.2 kcal mol^{-1}, and both **2** and **3** decomposed to **1** and **4** under the reaction conditions. Thus, when **3** was heated with or without elemental sulfur under the same conditions, a mixture of **2** and **3** of in a ratio of about 20:1 was obtained together with **1**. Each thiirane also reacted with S_XCl_2 to form **2** and **4**. The isomerization and decomposition must be regarded as a side reaction of thiiranes to form other compounds that accompanies thiirane-ring opening, such as polymerization. In addition, using **1** in the study would facilitate the analysis of the reaction mixture by ^{1}H NMR. Thus, both the bridgehead hydrogens of 2-adamantylidene group in **1–4** and the axial hydrogens at 4-position of the group in **1, 2**, and **4** were affected by an anisotropic effect of the benzene ring in the 9-benzonorbornenylidene group, causing these hydrogen signals to appear at separated positions. Therefore, we concluded that **1** would be a model compound for research on suitable reaction conditions of the thiiranation of alkenes.

4,4′-Oligothiodimorpholine **5** is a reagent known to react with rubber on heating [18]. In particular, 4,4′-dithiodimorpholine **6** is a widely used and commercially available, inexpensive vulcanizing agent. If a Brønsted acid is present in a reaction medium, **5** would be activated without heating because of the presence of the basic nitrogen atoms adjacent to the sulfur atoms [19,20]. Therefore, a combination of **5** and the Brønsted acid would act as a sulfuration reagent for the thiiranation. Furthermore, replacement of the chlorine atom in S_XCl_2 with a 4-morpholino group would prevent formation of byproducts, such as **4**. In this study, we observed that **6** transformed over a long period of time into a mixture containing 4,4′-tetrathiodimorpholine **7** in the solid state. As the proportion of sulfur atoms in a vulcanizing agent becomes higher, its vulcanization-accelerating activity should increase. Here, we report thiiranation of **1** using **7** and a Brønsted acid. Decomposition of the resulting thiirane and the thiiranation using **6**, 4,4′-thiodimorpholine **8**, and 2-(4′-morpholinodisulfanyl) benzothiazole **9** are also reported.

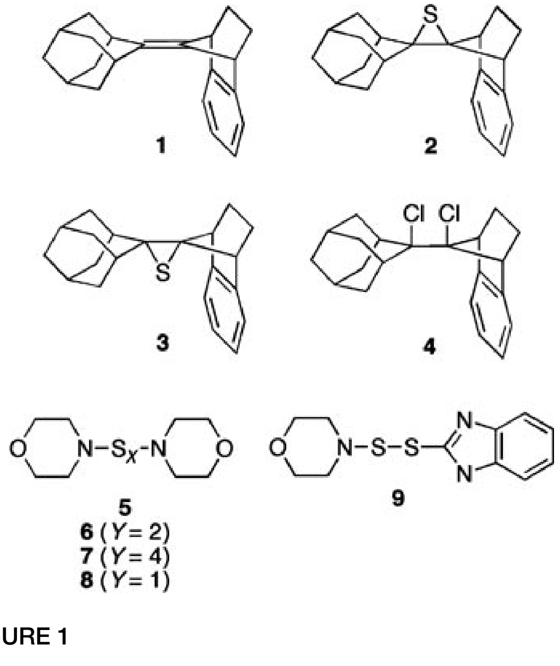


FIGURE 1

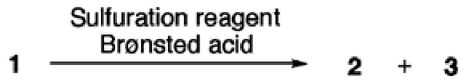
RESULTS AND DISCUSSION

Transformation of 4,4′-Dithiodimorpholine **6** *to 4,4′-Tetrathiodimorpholine* **7**

The 4,4′-dithiodimorpholine **6** mentioned in the Introduction section was gifted to our laboratory more than 10 years ago by Ouchi Shinko Chemical Industrial Co. Ltd. (Tokyo, Japan). During that time, the colorless powder **6** had changed slowly into a faint gray powdery mixture containing **7** [21], which was probably formed through disproportionation of **6** with the evolution of morpholine and the related volatile molecules, at room temperature for a long time. In fact, both this mixture and a purchased sample of **6** had a subtle odor, similar to morpholine, at room temperature. When the aforementioned mixture was carefully crystallized several times from EtOH, **7** was obtained as faint yellow needles in a pure form. Pure **6** was obtained by recrystallization of the purchased **6** from EtOH as colorless needles [22]. Both **6** and **7** can be stored in a freezer at −18°C for several months without decomposition. Attempted syntheses of **7** from **6** in the solid state failed. Thus, two processes were tested: heating **6** at 120°C/24 mmHg in a Kugelrohr distillation apparatus to remove the volatile materials and heating around its melting point under oxygen atmosphere. Both resulted in the quantitative recovery of **6**.

Thiiranation of 2′-Adamantylidene-9-Benzonorbornenylidene **1** *with 4,4′-Tetrathiodimorpholine* **7** *and Brønsted Acid*

A combination of **7** and carboxylic acid or sulfonic acid was used for the thiiranation of **1** (Scheme 1);



SCHEME 1

TABLE 1 Reactions of **1** with **7** and Brønsted Acids[a]

Entry	*Brønsted Acid*	*Conditions*	*Yield (%)*[b] **2**	**3**	**1**
1	CF_3CO_2H	CH_2Cl_2, r. t., 26 h	53	29	17
2	CH_3CO_2H	CH_2Cl_2, r. t., 26 h	–	–	Quant.
3	CHF_2CO_2H	CH_2Cl_2, r. t., 240 h	9	3	88
4	$NCCH_2CO_2H$	CH_2Cl_2, r. t., 720 h	15	Trace	85
5	$NCCH_2CO_2H$	CH_2Cl_2, reflux, 24 h	21	29	50
6	$NCCH_2CO_2H$	CH_2Cl_2, reflux, 16 h	15	12	73
7	p-TsOH·H_2O	CH_2Cl_2, r. t., 50 h	42	43	14

[a] **7** (0.4 molar equivalent), Brønsted acid (0.5 molar equivalent).
[b] By ^1H NMR.

TABLE 2 Effect of a Molar Ratio of **7** and Brønsted Acid on the Formations of **2** and **3**[a]

Entry	*Molar Equivalent of 7*	*Brønsted Acid (Molar Equivalent)*	*Time (days)*	*Yield (%)*[b] **2**	**3**	**1**
1	1.0	CF_3CO_2H (1.0)	5	Quant.	–	–
2	1.0	CHF_2CO_2H (1.0)	11	23	65	12
3	1.0	$NCCH_2CO_2H$ (1.0)	11	23	48	19
4	1.0	p-TsOH·H_2O (1.0)	5	61	28	11
5	1.0	CF_3CO_2H (0.5)	2	Quant.	–	–
6	1.0	CHF_2CO_2H (0.5)	6	27	44	29
7	1.0	$NCCH_2CO_2H$ (0.5)	6	20	27	54
8	1.0	p-TsOH·H_2O (0.5)	6	31	22	48
9	0.5	CF_3CO_2H (0.5)	5	94	2	5
10	0.5	CHF_2CO_2H (0.5)	7	26	43	31
11	0.5	$NCCH_2CO_2H$ (0.5)	7	13	39	48
12	0.5	p-TsOH·H_2O (0.5)	7	37	38	26
13	0.33	CF_3CO_2H (0.5)	7	27	38	36
14	0.33	CHF_2CO_2H (0.5)	7	26	41	33
15	0.33	$NCCH_2CO_2H$ (0.5)	7	20	27	53
16	0.33	p-TsOH·H_2O (0.5)	7	44	27	29
17	0.33	CF_3CO_2H (0.33)	7	65	5	30
18	0.33	CHF_2CO_2H (0.33)	7	17	35	48
19	0.33	$NCCH_2CO_2H$ (0.33)	7	11	28	61
20	0.33	p-TsOH·H_2O (0.33)	7	26	17	57

[a] In CH_2Cl_2 at r. t.
[b] By ^1H NMR.

the results are summarized in Table 1. The thiiranation with CF_3CO_2H ($pK_a = 0.23$) [23] in CH_2Cl_2 for 26 h gave **2** and **3** in 53% and 29% yields, respectively, together with **1** in 17% yield (entry 1). When CH_3CO_2H ($pK_a = 4.76$) [23] was used under the same conditions, **1** was recovered quantitatively (entry 2). Using CHF_2CO_2H ($pK_a = 1.24$) [23] or $NCCH_2CO_2H$ ($pK_a = 2.43$) [23] brought about slow progress of the thiiranation (entries 3 and 4). These results suggest that increasing a pK_a value of carboxylic acids tends to decrease the yields of the thiiranes. The thiiranation with $NCCH_2CO_2H$ in refluxing CH_2Cl_2 gave **2** and **3** in a moderate total yield (entry 5), but raising the reaction temperature above 84°C (the boiling point of (CH_2Cl_2) inhibited the thiirane formation (entry 6). Overheating of the reaction mixture would lead to decomposition of the products. On the other hand, p-TsOH·H_2O ($pK_a = -1.7$) [24] acted as a good activating agent in a similar way to CF_3CO_2H (entry 7).

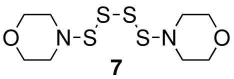
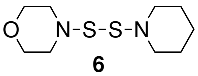
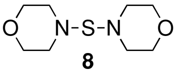
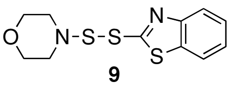
Effect of Molar Ratios of 7 *and Brønsted Acids*

We studied effect of the molar ratios of the **7** and the Brønsted acids on the thiiranation (Table 2). The reactions of **1** with 1.0 molar equivalent of **7** and the Brønsted acid each gave **2** and **3** in a good total yield (entries 1–4). The yields of the thiiranes decreased when 0.5 molar equivalent of the Brønsted acid was used (entries 5–8). An exception was CF_3CO_2H, which led to the quantitative formation of **2**. Diminishing the quantities of **7** and the carboxylic acid to 0.5 molar equivalents each did not affect the yields of the products (entries 9–11). In contrast, using 0.5 molar equivalents of **7** and p-TsOH·H_2O each caused a slight improvement in the yield of **3** compared with using 1.0 molar equivalent of **7** and 0.5 molar equivalent of p-TsOH·H_2O (entry 12). When 0.33 molar equivalent of **7** was used, the total yield of **2** and **3** decreased but was between 39% and 71% (entries 13–20). These results reveal that although decreasing the quantity of **7** tended to decrease the yields of the thiranes, more than one sulfur atom in **7** was introduced into the products. In the reactions with any Brønsted acid, using an equimolar amount of **7** and the Brønsted acid against **1** produced the best result for the thiirane formations.

Thiiranation of 1 *with Other Sulfuration Reagent and Brønsted Acid*

The reactions with **6**, 4,4′-thiodimorpholine **8** [21], and 2-(4′-morpholinodisulfanyl) benzothiazole **9** were investigated (Table 3). In case of using any Brønsted acid, decreasing the sulfur atoms in the oligothiodimorpholines tended to decrease the production of **2** and **3** (entries 1–11). Under these reaction conditions, 4,4′-thiodimorpholine **8** was much less reactive than **7** and **6**. The compound **9** also reacted with **1** in the presence of the Brønsted acids to give the thiiranes (entries 12–15). The ratio of the thiiranes and the recovered **1** in these reactions was similar to that in the reactions using **6.** Therefore, the order of reactivity of the sulfuration reagents combined with a Brønsted acid is **7**>**6** ~ **9**>**8**.

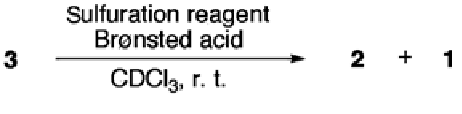
TABLE 3 The Reactions with **6–9** and Brønsted Acids[a]

Entry	*Sulfuration Reagent*	*Brønsted Acid*	*Time (days)*	*Yield (%)*[b]		
				2	**3**	**1**
1	 **7**	CF_3CO_2H	5	Quant.	–	–
2		CHF_2CO_2H	11	23	65	12
3		$NCCH_2CO_2H$	11	33	48	19
4		*p*-TsOH·H_2O	5	61	28	11
5	 **6**	CF_3CO_2H	5	36	10	54
6		CHF_2CO_2H	11	12	26	63
7		$NCCH_2CO_2H$	11	8	11	81
8		*p*-TsOH·H_2O	5	9	13	78
9	 **8**	CF_3CO_2H	7	13	5	82
10		CHF_2CO_2H	7	3	5	92
11		*p*-TsOH·H_2O	7	2	3	95
12	 **9**	CF_3CO_2H	7	41	17	42
13		CHF_2CO_2H	7	6	12	82
14		$NCCH_2CO_2H$	7	7	4	89
15		*p*-TsOH·H_2O	7	26	15	62

[a] Sulfuration reagent (1.0 molar equivalent), Brønsted acid (1.0 molar equivalent), in CH_2Cl_2 at r. t.
[b] By ^{1}H NMR.

Decomposition of the Thiirane **3** *Under the Thiiranation Conditions*

When the reactions of **1** with **7** and CF_3CO_2H that resulted in the quantitative formation of **2** were monitored by thin-layer chromatgraphy (TLC), in some cases, two spots due to the thiiranes were observed in the initial stage of the reaction and then the spot due to **2** enlarged and the other due to **3** disappeared. This probably means that **3** easily isomerizes to **2** and decomposes to **1** under these conditions. Therefore, we monitored the reactions of **3** with the sulfuration reagents (1.0 molar equivalent) and Brønsted acids (1.0 molar equivalent) in $CDCl_3$ with ^{1}H NMR (Scheme 2). When **3** reacted with 4,4′-tetrathiodimorpholine **7** and CF_3CO_2H for 15 h, **3** transformed to **2** quantitatively. As the pK_a value of the carboxylic acid used was increased, the consumption of **3** slowed. Thus, the reactions with CHF_2CO_2H and $NCCH_2CO_2H$ were still in progress after 15-h reaction time (Figs. 2a and 2b). The decomposition of **3** proceeded rapidly in the initial stage, and then, both **1** and **3** were gradually consumed and the formation of **2** increased as time went by (CHF_2CO_2H after 15 min: **2**, 33%; **1**, 20%; **3**, 46%; after 1 h: **2**, 61%; **1**, 13%; **3**, 26%; after 3 h: **2**, 66%; **1**, 10%; **3**, 24%; after 1 day: **2**, 81%; **1**, 7%; **3**, 12%; $NCCH_2CO_2H$ after 20 min: **2**, 5%; **1**, 22%; **3**, 73%; after 2 h: **2**, 23%; **1**, 22%; **3** 73%; after 8 h: **2**, 28%; **1**, 21%; **3** 51%; after 1 day: **2**, 34%; **1**, 18%; **3** 48%), suggesting that the resulting alkene **1** is sulfurated to form **2** and **3** under these reaction conditions. The reaction with *p*-TsOH·H_2O for 16 h gave **2**, **1**, and **3** in 15%, 10%, and 45% yields, respectively. Allowing more time for the reaction resulted in no change of the product ratio (after 32 h: **2**, 45%; **1**, 10%; **3**, 45%).



SCHEME 2

Using **6** instead of **7** brought about a slower consumption of **3**. Thus, when CF_3CO_2H was used, 56% of **3** still existed even after a reaction time of 1 day, and **2** and **1** were produced in 16% and 28% yields, respectively (Fig. 2c). In the case of CHF_2CO_2H, 79% of **3** remained after 3 days (Fig. 2d). In both the reactions, the consumption of **3** seemed to proceed only in the initial stage (CF_3CO_2H after 15 min: **2**, 8%; **1**, 25%; **3**, 67%; after 3 h: **2**, 11%; **1**, 29%; **3**, 60%; after 1 day: **2**, 16%; **1**, 28%; **3** 56%; CHF_2CO_2H after 1 h: **2**, 5%; **1**, 13%; **3**, 82%; after 4 h: **2**, 3%; **1**, 15%; **3**, 82%; after 8 h: **2**, 3%; **1**, 15%; **3**, 82%; after 3 days: **2**, 6%; **1**, 15%; **3** 79%). The reaction with $NCCH_2CO_2H$ for 5 days led to the quantitative recovery of **3**. When *p*-TsOH·H_2O was used, only a slight decomposition of **3** to **1** was observed in the initial stage (after 1 h: **2**, none; **1**, 7%; **3**, 93%; after 3 days: **2**, none; **1**, 3%; **3**, 97%). Consequently, a combination of **6** and $NCCH_2CO_2H$ or *p*-TsOH·H_2O is considered to be better for preventing both the isomerization

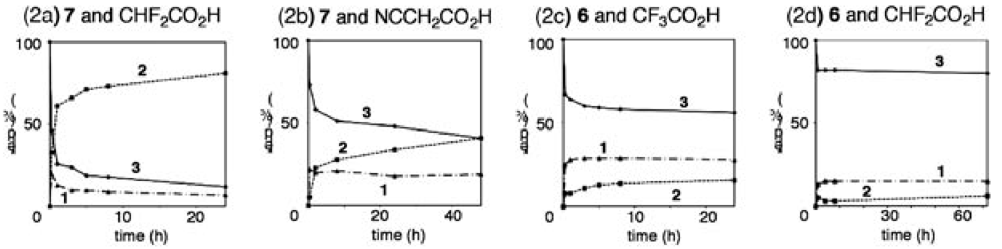
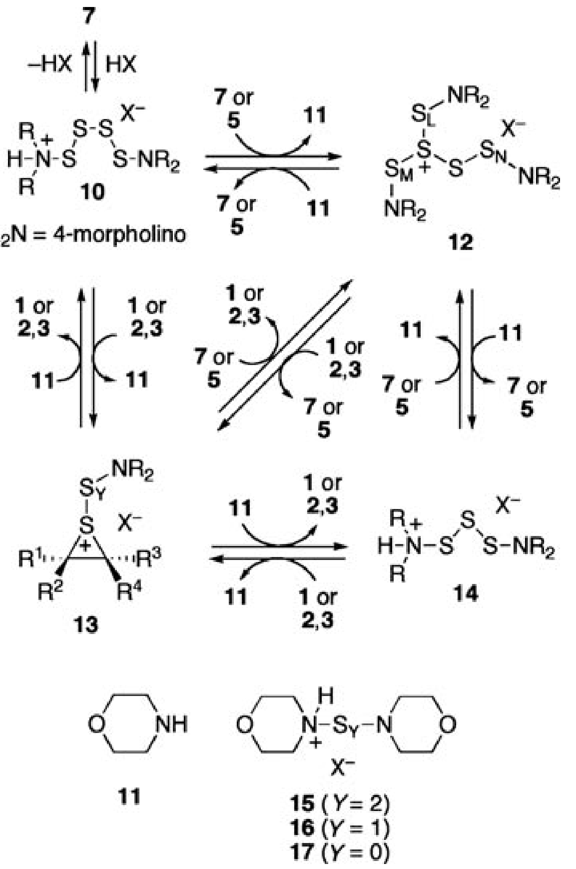


FIGURE 2 Diachronic change of product yields in the reaction of **3** with the sulfuration reagent and carboxylic acids. Sulfuration reagent (1.0 molar equivalent), Brønsted acid (1.0 molar equivalent) in CDCl$_3$ at r. t. By ^{1}H NMR.

and decomposition of **3** than other combinations. However, the combinations unfortunately did not produce satisfactory results for the thiiranation.

Possible Mechanism of the Thiiranation

The possible mechanism of the thiiranation of **1** and the decomposition of **3** is as follows (Scheme 3). One of the basic nitrogen atoms of **7** is protonated by a Brønsted acid (HX) to give the ammonium salt **10**, which then reacts with **7** to form morpholine **11** and the sulfonium salt **12**. The reactions of **1** with **10** and **12** gives the thiiranium salt **13**, which is also produced by the reactions of **2** and **3**, together with **11** in the case of **10**, and 4,4′-oligothiodimorpholine **5** in the case of **12**. The sulfonium salt **12** may be less reactive to **3** than **10**, so that the drastic decomposition of **3** proceeds in the initial stage of the reaction. A substitution reaction at the sulfur atom next to the positively charged sulfur atom in **13** with **11** takes place to give **2, 3**, and the ammonium salt **14**, which also reacts with **7** to form **12** and **11**. These sequential processes are reversible and, therefore, the decomposition of **3** to **1** proceeds. Thus, the substitution reaction at the positively charged sulfur atom in **13** with **7** or **11** affords **1**. The similar processes for the reaction of **1** with **14, 15**, or **16** lead to the formation of **2** and **3**, together with **15, 16**, or **17**. The ammonium salt **15** or **16** is also produced by the reaction of **6** or **8** with a Brønsted acid. The reason why the thiiranation becomes slower as the number of sulfur atoms in **5** decreases must be that steric congestion around the reactive sulfur atom in the ammonium salts and **12** increases and electronic repulsions among their lone pairs of the nitrogen and sulfur atoms decrease.



SCHEME 3

Two mechanisms of the isomerization of **3** to **2** are possible. One includes the reverse pathway of the thiirane formation mentioned above, which results in the formation of **1**, followed by the resulfuration of **1**. The other contains five sequential reversible processes: (1) formation of **18**, (2) cleavage of the C—S bond close to the 9-benzonorbornenylidene group to give intermediates **19**, which is stabilized by neighboring-group participation of the benzene ring, (3) rotation about the central C—C bond, (4) recombination of the C—S bond in **20** to form **21**, and (5) removal of the ammonium salt like **10** and the sulfonium salt **12** to form the thermally more stable **2** rather than **3** [13,14].

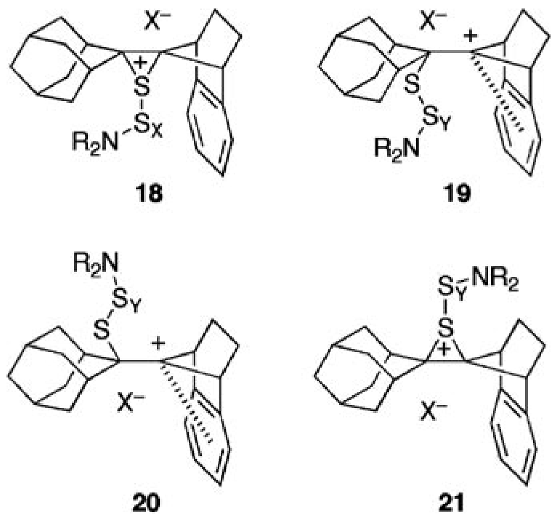


FIGURE 3

EXPERIMENTAL

Solvents were dried and purified in the usual manner. 4,4′-tetrathiodimorpholine **7** was recrystallized several times from EtOH. 4,4′-dithiodimorpholine **6** was purchased from Tokyo Chemical Industry (Tokyo, Japan) and purified by recrystallization from EtOH. 4,4′-thiodimorpholine **8** was prepared and purified by the literature method [21]. 2-(4′-morpholinodisulfanyl) benzothiazole **9** was gifted from Ouchi Shinko Chemical Industrial and purified by recrystallization from EtOH. All the reactions were carried out under argon. Silica gel column chromatography was performed on silica gel 60N (Kanto, 63–210 μm, spherical, neutral). Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AC300P (300.1 MHz for ^{1}H) or a Bruker AC200 (200.1 MHz for ^{1}H and 50.3 MHz for ^{13}C) spectrometer using $CDCl_3$ as the solvent with TMS for ^{1}H and with $CDCl_3$ for ^{13}C as the internal standard. Elemental analyses were performed by the Molecular Analysis and Life Science Center of Saitama University.

4,4′-Tetrathiodimorpholine 7

Faint yellow needles (from EtOH), mp 121.2–121.8°C (mp 118.5–119.5°C) [21]; ^{1}H NMR (300.1 MHz) δ 3.03 (t-like, 8H), 3.74 (t-like, 8H); ^{13}C NMR (50.3 MHz) δ 55.7, 67.0; Anal. Calcd for $C_8H_{16}N_2O_2S_4$: C, 31.89; H, 5.37; N, 9.32. Found: C, 32.17; H, 5.28; N, 9.19.

4,4′-Dithiodimorpholine **6**

Colorless needles (from EtOH), mp 126.5–127.0°C (mp 124–125°C) [22]; ^{1}H NMR (300.1 MHz) δ 2.83 (t-like, 8H), 3.74 (t-like, 8H); ^{13}C NMR (50.3 MHz) δ 55.7, 67.2; Anal. Calcd for $C_8H_{16}N_2O_2S_2$: C, 40.65; H, 6.28; N, 11.85. Found: C, 40.89; H, 6.48; N, 11.74.

General Procedures for Sulfuration of **1** *with the Sulfuration Reagent and Brønsted Acid*

A solution of **1** (73–100 μmol), the sulfuration reagent, and Brønsted acid in solvent (2.0 mL) was allowed to stand at room temperature or was heated at reflux. The reaction was quenched by addition of aqueous $NaHCO_3$ solution. After CH_2Cl_2 was added to the mixture, the organic layer was separated, washed with H_2O, dried over K_2CO_3, and evaporated under reduced pressure. A ratio of the products was estimated by ^{1}H NMR.

General Procedures for Reaction of **3** *with the Sulfuration Reagent and Brønsted Acid*

A solution of **3** (7.7 mg, 25 μmol), the sulfuration reagent (25 μmol), Brønsted acid (25 μmol), and triptycene as an internal standard in $CDCl_3$ (0.50 mL) was allowed to stand at room temperature. Progress of the reaction was monitored by ^{1}H NMR.

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