Heteroatom Chemistry
Volume 13, Number 5, 2002

# Practical Synthesis of Thiirene 1-Oxides that Possess Two Bulky Alkyl Substituents

Juzo Nakayama, Kenta Takahashi, Yutaka Ono, Michiyo Morita, Yoshiaki Sugihara, and Akihiko Ishii

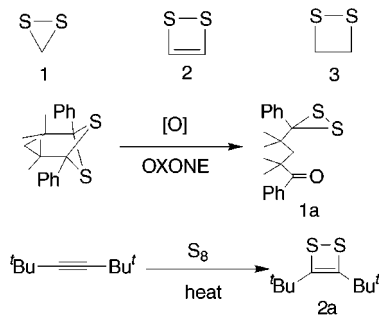
*Department of Chemistry, Faculty of Science, Saitama University, Saitama, Saitama 338-8570, Japan*

*Received 22 June 2001; revised 25 March 2002*

ABSTRACT: *Acetylenes that possess two bulky alkyl substituents reacted with sulfur dichloride to furnish the corresponding 2,3-dialkyl-2,3-dichlorothiiranes (***5***) nearly quantitatively. The alkaline hydrolysis of* **5** *afforded 2,3-dialkylthiirene 1-oxides (***10***) in high yields. These two reactions could be successively carried out in one flask, and 2,3-di-*tert*-butyl-, 2,3-di-(1-adamantyl)-, and 2-(1-adamantyl)-3-*tert*-butylthiirene 1-oxides (***10a–c***) were obtained in 70, 80, and 90% yields, respectively, based on the starting acetylenes, thus providing the most convenient synthesis of thiirene 1-oxides. Disulfur dichloride also reacted with acetylenes to give* **5** *in good yields with the elimination of one sulfur atom. Although the alkaline hydrolysis of* **5** *provided* **10** *exclusively, acid hydrolysis gave a mixture of α-oxothioketone* **9** *and thiirene 1-oxide* **10** *in modest yields. All thiirene 1-oxides* **10a–c** *isomerized to produce α-oxothioketones* **9** *in high yields when heated in boiling toluene. Reactions of a bis-acetylene (***18***) with disulfur dichloride and with sulfur dichloride gave a dihydropentathiepin (***19***) in high yields.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:424–430, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10070

## *INTRODUCTION*

Our recent interests involve the chemistry of small ring compounds such as dithiiranes (**1**), 1,2-dithietes (**2**), and 1,2-dithietanes (**3**), containing a disulfide bond Quite recently, we have reviewed the chemistry of these compounds [1]. In 1994, we succeeded in performing the synthesis of dithiirane **1a** [2]. This is the first dithiirane which was isolated in pure form and whose structure was determined by X-ray diffraction analysis. We also synthesized a series of 1,2-dithietes by sulfuration of acetylenes with elemental sulfur [3]. For example, heating di-*tert*-butylacetylene with elemental sulfur at about 200°C afforded dithiete **2a** in good yield.



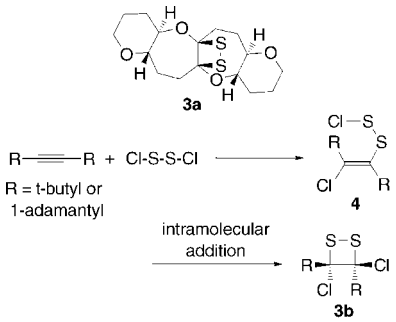

Thus, only 1,2-dithietanes remain to be synthesized. Compound **3a** is the only isolable 1,2-dithietane reported by Nicolaou et al. [4]. We chose the reaction of acetylenes with disulfur dichloride for the preparation of 1,2-dithietanes. This sulfur reagent would add acetylenes to give adducts **4**. If we use an acetylene that possesses bulky substituents, such as *tert*-butyl and 1-adamantyl, addition of **4** to

This paper is dedicated to the late Professor Shigeru Oae who devoted his life to the development of heteroatom chemistry.

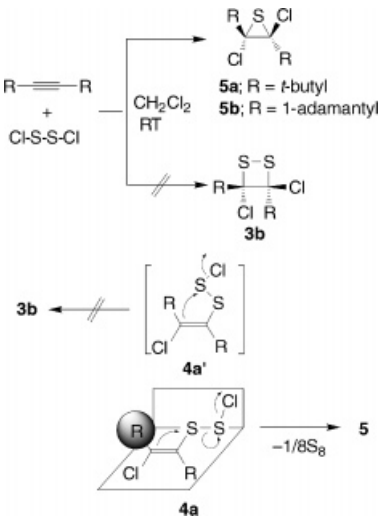
*Correspondence to:* Juzo Nakayama; e-mail: nakaj@post.saitama-u.ac.jp.

Contract grant sponsor: Ministry of Education, Science, Sports, Culture, and Technology.
Contract grant number: 13029016.

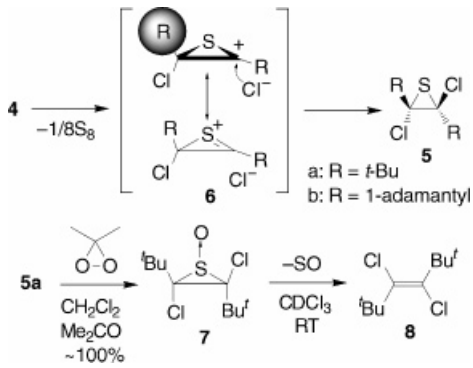
another molecule of the acetylene would be disfavored sterically. As a result, an intramolecular reaction would take place to give 1,2-dithietane **3b** [5].



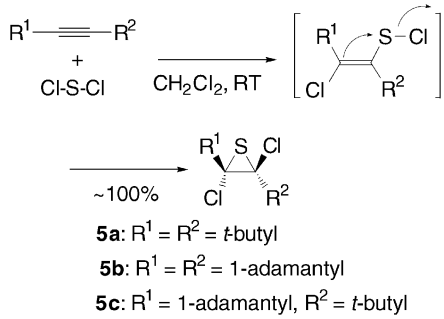

Thus, di-*tert*-butyl- and di-1-adamantylacetylenes were allowed to react with disulfur dichloride at room temperature. Unexpectedly, the reaction afforded the dichlorothiiranes **5** in good yields. The expected 1,2-dithietane **3b** was not formed even in trace amounts. To our knowledge, this is the first synthesis of dihalosubstitued thiiranes. Thiiranes **5** are sensitive to hydrolysis. Compound **5a** was isolated in pure form by distillation whereas **5b**, which could not be purified by distillation, was hydrolyzed during attempted purification by silica-gel column chromatography discussed later. The initial step of the present reaction would be the addition of disulfur dichloride to the acetylenes that produce the expected adducts **4**. The preferable conformation of **4** would be **4a**, and not **4a′**, so as to avoid the steric repulsions between the bulky substituent R and the SCl group. Therefore, the sulfur atom (bearing a chlorine atom) and the $sp^2$ carbon atom (bearing a chlorine atom) are too remote to interact, and hence the four-membered ring formation that leads to **3b** is disfavored. As a result, exclusive three-membered ring formation takes place to give **5** with the elimination of a sulfur atom.




The stereochemistry of thiiranes **5** is thought to be trans based on mechanistic grounds. Cyclization of the adduct **4** gives rise to the sulfur-stabilized carbocation **6**, and then the chloride ion adds to **4** to produce the less conjugated trans-product **5**. The trans-stereochemistry was established by an oxidation study. Thus, oxidation of thiirane **5a** with dimethyldioxirane afforded thiirane 1-oxide **7** in which two *tert*-butyl groups are nonequivalent in both their $^1H$ and $^{13}C$ NMR spectra. In the trans-case, the oxidation might give two isomeric thiirane 1-oxides. Even if a single thiirane 1-oxide was formed for steric reasons, its two *tert*-butyl groups would be equivalent. The thiirane 1-oxide **7** was thermally labile and decomposed slowly at room temperature to give the alkene **8** in good yield.

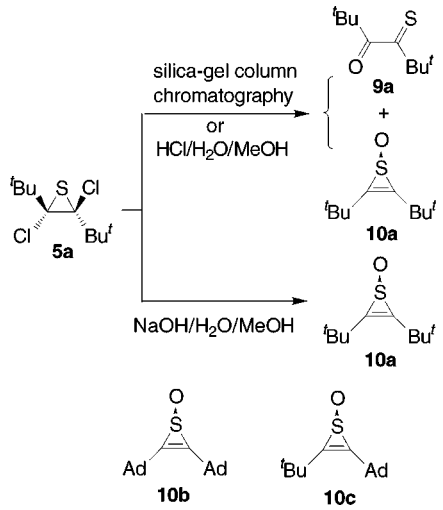



The above results inspired us to use sulfur dichloride in place of disulfur dichloride in the addition to alkynes. As expected, sulfur dichloride added to acetylenes to furnish thiiranes **5a–c** nearly quantitatively. No elemental sulfur is formed in this case. This makes the isolation procedure of **5** much easier; mere evaporation of the solvent provided **5** in practically pure form.

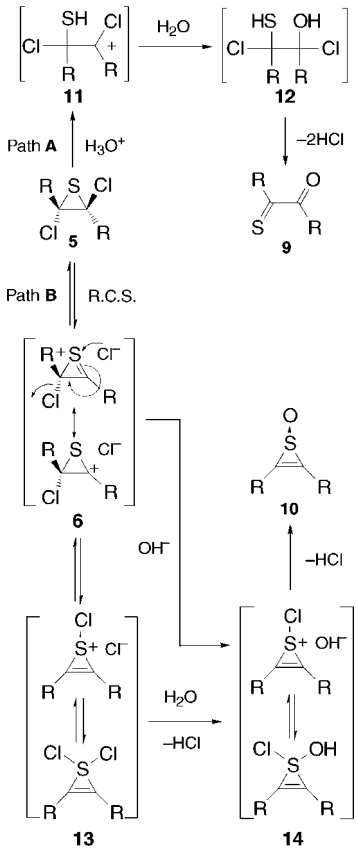



Throughout the above described study, we learned that the thiiranes **5** are sensitive to hydrolysis. For example, attempted purification of **5a** by

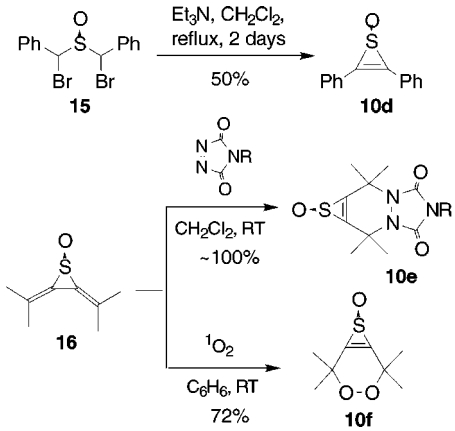
silica-gel column chromatography produced two hydrolized products, α-oxothioketone **9a** and thiirene 1-oxide **10a**, both in modest yields. HCl-catalyzed hydrolysis also produced both compounds in modest yields. The formation of the thiirene oxide **10a** is rather unexpected and is of particular interest. These results prompted us to examine alkaline hydrolysis, which led to the sole formation of **10a**. That is, the alkaline hydrolysis (NaOH in MeOH/$H_2O$) of **5a** provided **10a** exclusively in good yield. Similarly, alkaline hydrolyses of **5b** (NaOH in THF/$H_2O$) and **5c** (NaOH in EtOH/$H_2O$) gave the corresponding thiirene 1-oxides **10b** and **10c** in good yields.




The following are probable mechanisms of the hydrolyses. For the acid-hydrolysis, protonation of the sulfur atom of **5** would result in the ring-opening of the three-membered ring to produce a carbocation intermediate **11**. Addition of water to **11**, followed by the elimination of two molecules of HCl, afforded thioketone **9** (Path **A**). In competition with this pathway, **5** would dissociate into the sulfur-stabilized carbocation **6** (Path **B**). The carbocation **6** then isomerizes to a sulfonium ion or its isomeric sulfurane **13**. Replacement of Cl of **13** by OH produces **14**. Finally, the elimination of HCl from **14** provides thiirene 1-oxide **10** as the final product. Under the alkaline conditions, the Path **A** cannot work, and thus only Path **B** is operative to lead to the exclusive formation of **10**. In this case, **14** might be directly formed by addition of the hydroxide ion to **6**. The rate-controlling step of the alkaline hydrolysis would be the dissociation step of **5** into **6** because the hydrolysis was remarkably retarded by addition of chloride ion (NaCl).

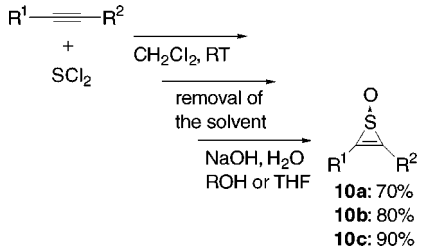



The first thiirene 1-oxide **10d** was synthesized from **15** in 50% yield by a modification of the Ramberg–Bäcklund reaction [6]. Later, the first dialkyl substituted thiirene 1-oxides **10e** [7a] and **10f** [7b] were synthesized in good yields by Diels–Alder reactions of a thiiranoradialene **16** with triazolinediones or with singlet oxygen. These methods, however, suffer from some disadvantages such as moderate yield, longer reaction time, and difficulty of obtaining the starting material. Efforts were then made to improve our synthetic method.

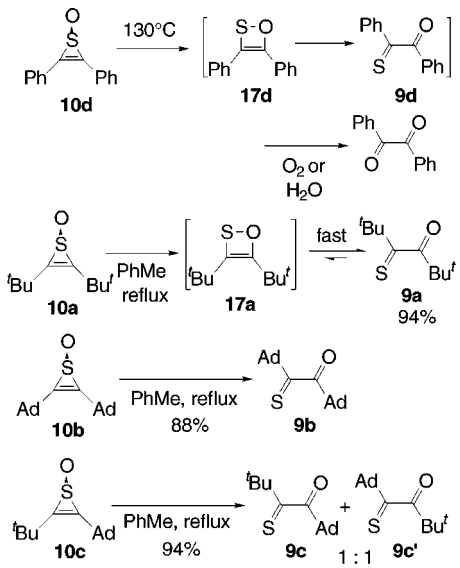



Thus, three acetylenes were allowed to react with an equimolar amount of sulfur dichloride at

room temperature, and then reaction mixtures were evaporated under reduced pressure. The resulting crude thiiranes were directly subjected to alkaline hydrolysis. In this way, 2,3-di-*tert*-butyl-, 2,3-di-1-adamantyl-, and 2-adamantyl 3-*tert*-butylthiirene oxides **10a–c** were obtained in 70, 80, and 90% overall yields, respectively, based on the starting acetylenes. These are practically one-flask reactions, and thus provide a most convenient synthesis of thiirene 1-oxides.

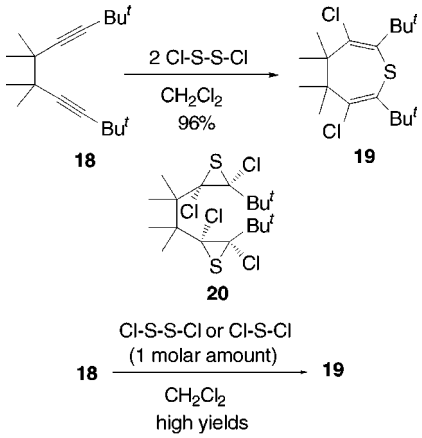



It was reported that the thiirene 1-oxide **10d** produced benzil on thermolysis [6b]. Ring-expansion of **10d–17d** and air-oxidation or hydrolysis of α-oxothioketone **9d** that forms by ring-opening of **17d** were proposed to explain the formation of benzil. All the 1-oxides **10a–c** isomerized in high yields to give the corresponding α-oxothioketones **9a–c** when heated in boiling toluene. For the unsymmetrically substituted thiirene 1-oxide **10c**, two isomeric α-oxothioketones **9c** and **9c′** were formed in a 1:1 ratio. Expected intermediates 1,2-oxathietes, such as **17a**, were neither isolated nor detected by $^1$H NMR spectroscopy probably because the ring-opening of 1,2-oxathietes to α-oxothioketones takes place quickly; in other words, the equilibrium between 1,2-oxathietes and α-oxothiketones lies far to the latter side [3c,8].




Application of the reaction of acetylenes with disulfur dichloride to the bis-acetylene **18** [3a] provided the dihydropentathiepine **19** in 96% yield. The expected bis-thiirane **20** did not form. Even 1 M of disulfur dichloride or sulfur dichloride also gave **19** in high yields.

Reactions of bis(trimethylsilyl)acetylene and *tert*-butylphenylacetylene with sulfur dichloride gave complex mixtures from which expected thiiranes could not be isolated.




In conclusion, we have developed a high-yield synthesis of thiirene 1-oxides that possess bulky alkyl substituents. The method is practically a one-flask reaction, and thus provide a most convenient synthesis of thiirene 1-oxides.

## *EXPERIMENTAL*

Solvents were purified and dried in the usual manner. All of the reactions were carried out under argon. Silica-gel column chromatography was performed on silica gel 7734 (Merck, 70-230 mesh). 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 ARX400, a Bruker AM400, a Bruker AC300P, or a Bruker AC200 spectrometer by using $CDCl_3$ as the solvent with TMS as the internal standard. IR spectra were taken on a Hitachi 270-50 or a Perkin-Elmer System 2000 FT-IR spectrometer. The UV spectrum was determined on a JASCO V-560 spectrophotometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. Di-*tert*-butyl- and di-(1-adamantyl)acetylenes [9], 1-adamantyl-*tert*-butylacetylene [10], and 2,2,5,5,6,6,9,9-octamethyldeca-3,7-diyne (**18**) [3a] were prepared according to the literature methods.

### *Preparation of 2,3-Dialkyl-2,3-dichlorothiiranes* **5a–c** *from Acetylenes and $SCl_2$*

To a stirred solution of an acetylene (1 mmol) in $CH_2Cl_2$ (7 ml) was added slowly a solution of $SCl_2$ (1.2–1.5 mmol) in $CH_2Cl_2$ (3 ml). After the mixture had been stirred for 5 h at room temperature, the reaction was quenched by addition of 1 M NaOH (3 ml). The organic layer was washed with water, dried over $MgSO_4$, and evaporated to give crude compounds **5**, which were purified by distillation or crystallization.

*(E)-2,3-Di-tert-butyl-2,3-dichlorothiirane (***5a***).* b.p. 72°C/5 mm Hg (pot-to-pot distillation); $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.39 (18H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz): $\delta$ 29.6, 44.7, 85.6; IR (film): 2972, 2936, 2876, 1484, 1466, 1398, 1368, 1210, 732, 702 cm$^{-1}$. Anal calcd for $C_{10}H_{18}Cl_2S$: C, 49.79; H, 7.52. Found: C, 49.87; H, 7.57.

*(E)-2,3-Di-(1-adamantyl)-2,3-dichlorothiirane (***5b***).* m.p. 181–186°C; $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.66–1.68 (12H, m), 2.06–2.08 (6H, m), 2.14–2.17 (12H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz): $\delta$ 29.4, 36.7, 39.8, 46.2, 85.2; IR (KBr): 2908, 2852, 1450, 1372, 1358, 1342, 1304, 1260, 1188, 1102, 1074, 1058, 976, 948 cm$^{-1}$. Anal. calcd for $C_{22}H_{30}Cl_2S$: C, 66.48; H, 7.61. Found: C, 66.22; H, 7.63.

*(E)-2-(1-Adamantyl)-3-tert-butyl-2,3-dichlorothiirane (***5c***).* Colorless needles; m.p. 118–119°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 1.39 (9H, s), 1.65–1.67 (6H, m), 2.06 (3H, m), 2.13 (6H, m); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ 29.3, 30.0, 36.6, 39.5, 45.8, 85.2, 85.6; IR (KBr): 2972, 2908, 2852, 1478, 1450, 1396, 1364, 1344, 1310, 1266, 1206, 1186, 1164, 1100, 1070, 1028, 976 cm$^{-1}$. Anal. calcd for $C_{16}H_{24}Cl_2S$: C, 60.18; H, 7.58. Found: C, 60.06; H, 7.60.

### *One-Flask Synthesis of Thiirene 1-Oxides* **10a–c**

A solution of 159 mg (1.5 mmol) of $SCl_2$ in $CH_2Cl_2$ (3 ml) was added slowly to a stirred solution of 131 mg (1.0 mmol) of di-*tert*-butylacetylene in $CH_2Cl_2$ (7 ml) at room temperature. After the mixture had been stirred for 2 h, the solvent was removed under reduced pressure. The resulting crude **5a** was dissolved in 10 ml of MeOH. After 1 M NaOH (1 ml) had been added to the solution, the mixture was stirred for 5.5 h at room temperature. The resulting mixture was extracted with ether. The ether extracts were washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel (40 g). Elution of the column with hexane/AcOEt (4:1) gave 20 mg (11%) of 2,2,5,5-tetramethyl-4-oxohexane-3-thione (**9a**) [8], a red-purple oil; [$^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 1.27 (9H, s), 1.39 (9H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz): $\delta$ 28.6, 30.3, 42.1, 51.1, 212.9 (C=O), 270.1 (C=S)] and 124 mg (70%) of **10a**. The hydrolysis of purified **5a** under the same conditions gave **10a** as the sole product. The alkaline hydrolysis of the crude **5b**, carried out at room temperature for 17 h by using THF as the solvent because **5b** is hardly soluble in MeOH, gave **10b** in 80% yield, while that of **5c**, carried out in EtOH for 11 h at room temperature, gave **10c** in 90% yield.

*2,3-Di-tert-butylthiirene 1-Oxide (***10a***).* Faint-yellow crystals (from pentane); m.p. 35–37°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 1.40 (s); $^{13}$C NMR ($CDCl_3$, 50 MHz): $\delta$ 29.0, 32.9, 145.1; IR (film) 2970, 2932, 2870, 1478, 1461, 1366, 1080, 1066 (S=O), 1028, 753 cm$^{-1}$. Anal calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74. Found: C, 64.47; H, 9.78.

*2,3-Di-(1-adamantyl)thiirene 1-Oxide (***10b***).* Colorless crystals (from hexane); m.p. 162–167°C (dec); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.78 (12H, broad s), 1.93–2.05 (12H, m), 2.09–2.11 (6H, m); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ = 27.7, 34.5, 36.0, 40.9, 143.8; IR (KBr) 2904, 2848, 1456, 1364, 1342, 1316, 1258, 1102, 1062 (S=O), 1038 cm$^{-1}$. Anal calcd for $C_{22}H_{30}OS$: C, 77.14; H, 8.83. Found: C, 77.06; H, 8.85.

*2-(1-Adamantyl)-3-tert-butylthiirene 1-Oxide (***10c***).* Colorless granules (from pentane); m.p. 34–36°C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.39 (9H, s), 1.75–1.82 (6H, m), 1.95–2.07 (6H, m), 2.10–2.11 (3H, m); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ 27.9, 29.0, 32.8, 34.8, 36.2, 41.0, 144.2, 144.9; IR (KBr) 2972, 2908, 2852, 1478, 1456, 1366, 1078 (S=O), 988 cm$^{-1}$. Anal calcd for $C_{16}H_{24}OS$: C, 72.67; H, 9.15. Found: C, 72.76; H, 9.26.

### *Preparation of 2,3-Di-tert-butyl-2,3-dichlorothiirane (***5a***) from Di-tert-butylacetylene and $S_2Cl_2$ and Acid Hydrolysis*

To a stirred solution of 135 mg (1.0 mmol) of di-*tert*-butylacetyleme in $CH_2Cl_2$ (7 ml) was added slowly a solution of 142 mg of $S_2Cl_2$ (1.1 mmol) in $CH_2Cl_2$ (4 ml). After the mixture had been stirred for 5 h at room temperature, the reaction was quenched by addition of 1 M NaOH (3 ml). The organic layer was washed with water, dried over $MgSO_4$, and evaporated to give crude thiirane **5a** contaminated with elemental sulfur. Purification of the crude product by pot-to-pot distillation provided 131 mg (56%) of pure

**5a** (b.p. 80°C/23 mm Hg); distillation caused some decomposition of **5a**, thus leaving a considerable amount of a viscous oily pot residue. Meanwhile, attempted purification of the crude **5a**, obtained in the same scale reaction, by silica-gel column chromatography gave 67 mg (37%) of **9a** and 19 mg (10%) of **10a**. When 60 mg of purified **5a** was passed through a column of silica gel, it was hydrolyzed to give 20 mg (43%) of **9a** and 13 mg (28%) of **10a**. The hydrolysis of 103 mg of purified **5a** in a mixture of 0.5 ml of 3 M HCl and 4 ml of MeOH at room temperature for 5.5 h produced 28 mg (35%) of **9a** and 8 mg (10%) of **10a**.

### *Silica Gel-Catalyzed Hydrolysis of Crude Thiirane* **5b**

The crude thiirane **5b**, which was obtained by the reaction of 108 mg (0.4 mmol) of di-(1-adamantyl)-acetylene and 84 mg (0.6 mmol) of $S_2Cl_2$ in $CH_2Cl_2$ at room temperature for 5 h, was chromatographed on a column of silica gel (40 g) with hexane/AcOEt (4:1) as the eluent to give elemental sulfur, 25 mg (19%) of 3,4-di(1-adamantyl)dithiete, 6 mg (5%) of 1,2-di-(1-adamantyl)-2-oxoethanethione (**9b**), and 38 mg (30%) of 2,3-di-(1-adamantyl)thiirene 1-oxide (**10b**). The structure of 3,4-di(1-adamantyl)dithiete was determined by comparison of $^1$H and $^{13}$C NMR data with those of an authentic sample [3]. Compound **9b** was obtained as red-purple needles (from hexane) with a m.p. of 100–103°C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.71–1.72 (12H, m), 1.93–1.94 (3H, m), 2.01–2.06 (15H, m); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ 28.0, 28.4, 36.1, 36.3, 39.8, 42.0, 44.3, 53.6, 211.3 (C=O), 269.4 (C=S); IR (KBr): 2918, 1669 (C=O), 1211, 1165, 1104, 1027 cm$^{-1}$. Anal calcd for $C_{22}H_{30}OS$: C, 77.14; H, 8.83. Found: C, 76.96; H, 8.94.

### *(E)-2,3-Di-tert-butyl-2,3-dichlorothiirane 1-Oxide (***7***) and its Decomposition to (E)-1,2-Di-tert-butyl-1,2-dichloroethene (***8***)*

To a solution of 51 mg (0.2 mmol) of the thiirane **5a** in 3 ml of $CH_2Cl_2$ was added slowly 3 ml (0.3 mmol) of a 0.08 M solution of dimethyldioxirane in $Me_2CO$ at −18°C. After the mixture had been stirred for 2.5 h at −18°C, the solvent was removed under reduced pressure to give 51 mg (95%) of 1-oxide **7** as the single product. When a $CDCl_3$ solution containing compound **7** was allowed to stand at room temperature for several days, complete decomposition of **7** took place to give 36 mg (88%) of alkene **8** [11]. (*E*)-2,3-Di-*tert*-butyl-2,3-dichlorothiirane 1-oxide (**7**) was obtained as colorless oil; $^1$H NMR ($CDCl_3$, 400 Mz): $\delta$ 1.35 (9H, s), 1.50 (9H, s); $^{13}$C NMR ($CDCl_3$, 100.6 Mz): $\delta$ 29.6, 29.9, 42.2, 44.6, 81.3, 86.8. (*E*)-1,2-Di-*tert*-butyl-1,2-dichloroethene (**8**): $^1$H NMR ($CDCl_3$, 400 Mz): $\delta$ 1.37 (18H, s); $^{13}$C NMR ($CDCl_3$, 100.6 Mz): $\delta$ 29.9, 44.7, 137.1.

### *Thermal Isomerization of Thiirene 1-Oxides* **10a–c** *to α-Oxothiones* **9a–c**

Thiirene 1-oxides 10a, 10b, and 10c were heated in boiling toluene for 14.5, 30, and 15.5 h respectively. Toluene was removed under reduced pressure and the residue was chromatographed on a column of silica gel with hexane/AcOEt (4:1) as the eluent to furnish **9a** in 94%, **9b** in 88%, and a 1:1 mixture of **9c** and **9c′** in 94% yields. 1:1 mixture of **9c** and **9c′** was obtained as violet granules (from pentane) with m.p. of 64–66°C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.27 (9H, s), 1.38 (9H, s), 1.72–1.74 (12H, m), 1.96 (6H, m), 2.03 (9H, m), 2.09 (3H, m); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ 28.0, 28.4, 28.7, 30.4, 36.2, 36.4, 39.8, 41.9, 42.1, 44.4, 51.0, 53.8, 211.9 (C=O), 212.8 (C=O), 269.7 (C=S), 269.9 (C=S); IR (KBr): 2904, 2852, 1670, 1480, 1454, 1392, 1364, 1344, 1266, 1236, 1206, 1176, 1132, 1100, 1058, 894, 854 cm$^{-1}$. Anal calcd for $C_{16}H_{24}OS$: C, 72.67; H, 9.15. Found: C, 72.70; H, 9.30.

### *2,7-Di-tert-butyl-3,6-dichloro-4,4,5,5-tetramethyl-4,5-dihydrothiepin (***19***)*

A solution of 57 mg (0.4 mmol) of $S_2Cl_2$ in 3 ml of $CH_2Cl_2$ was added slowly to a solution of 51 mg (0.2 mmol) of 2,2,5,5,6,6,9,9-octamethyldeca-3,7-diyne (**18**) in 7 ml of $CH_2Cl_2$. After the mixture had been stirred for 8 h, the reaction was quenched by addition of 3 ml of 1 M NaOH. The organic layer was washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel with hexane as the eluent to give 69 mg (95%) of **19**. The use of an equivalent of $S_2Cl_2$ gave **19** in 80% yield with recovery of 17% of **18**. The use of $SCl_2$ in place of $S_2Cl_2$ also provided similar results. Compound **19** was obtained as colorless needles (from EtOH) with m.p. of 75.0–75.5°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 1.22 (s, 12H), 1.35 (s, 18H); $^{13}$C NMR ($CDCl_3$, 50 MHz): $\delta$ 22.6, 29.5, 40.3, 55.6, 127.5, 139.3; IR (KBr): 2966, 2866, 1482, 1396, 1221, 806 cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ ($\varepsilon$) 279 (10400), 263 (9120), 255 (9260), 250 (9440), 224 nm (3700). Anal calcd for $C_{18}H_{30}Cl_2S$: C, 61.87; H, 8.65. Found: C, 62.01; H, 8.76.

## *REFERENCES*

[1] Nakayama, J.; Ishii, A. Adv Heterocycl Chem 2000, 77, 221.

[2] (a) Ishii, A.; Akazawa, T.; Maruta, T.; Nakayama, J.; Hoshino, M. Angew Chem, Int Ed Engl 1994, 33, 777; For related reports, see (b) Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Nakayama, J.; Hoshino, M.; Shiro, M. J Am Chem Soc 1993, 115, 4914; (c) Ishii, A.; Jin, Y.-N.; Nagaya, H.; Hoshino, M.; Nakayama, J. Tetrahedron Lett 1995, 36, 1867; (d) Ishii, A.; Maruta, T.; Teramoto, K.; Nakayama, J. Sulfur Lett 1995, 18, 237; (e) Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Maruta, T.; Nakamura, S.; Nagaya, H.; Ogura, M.; Teramoto, K.; Shiro, M.; Hoshino, M.; Nakayama, J. Bull Chem Soc Jpn 1997, 70, 509; (f) Ishii, A.; Umezawa, K.; Nakayama, J. Tetrahedron Lett 1997, 38, 1431; (g) Ishii, A.; Nakamura, S.; Yamada, M.; Nakayama, J. Tetrahedron 1997, 53, 12203; (h) Jin, Y.-N.; Ishii, A.; Sugihara, Y.; Nakayama, J. Tetrahedron Lett 1998, 39, 3525; (i) Ishii, A.; Nakabayashi, M.; Jin, Y.-N.; Nakayama, J. J Orgnomet Chem 2000, 611, 127; (j) Ishii, A.; Kawai, T.; Tekura, K.; Oshida, H.; Nakayama, J. Angew Chem Int Ed Engl 2001, 40, 1924.

[3] (a) Nakayama, J.; Choi, K. S.; Akiyama, I.; Hoshino, M. Tetrahedron Lett 1993, 34, 115; For related papers, see (b) Choi, K. S.; Akiyama, I.; Hoshino, M.; Nakayama, J. Bull Chem Soc Jpn 1993, 66, 623; (c) Nakayama, J.; Mizumura, A.; Yokomori, Y.; Krebs, A.; Schütz, K. Tetrahedron Lett 1995, 36, 8583; (d) Nakayama, J.; Masui, N.; Sugihara, Y.; Ishii, A. Bull Chem Soc Jpn 1998, 71, 1181.

[4] (a) Nicolaou, K. C.; Hwang, C.-K.; Duggan, M. E.; Carroll, P. J. J Am Chem Soc 1987, 109, 3801; (b) Nicolaou, K. C.; Hwang, C.-K.; DeFrees, S.; Stylianides, N. A. J Am Chem Soc 1988, 110, 4868; (c) Nicolaou, K. C.; DeFrees, S. A.; Hwang, C.-K.; Stylianides, N.; Carroll, P. J.; Snyder, J. P. J Am Chem Soc 1990, 112, 3029.

[5] (a) Nakayama, J.; Takahashi, K.; Watanabe, T.; Sugihara, Y.; Ishii, A. Tetrahedron Lett 2000, 41, 8349; (b) Nakayama, J.; Takahashi, K.; Sugihara, Y.; Ishii, A. Tetrahedron Lett 2001, 42, 4017.

[6] (a) Carpino, L. A.; Chen, H.-W. J Am Chem Soc 1971, 93, 785; (b) Carpino, L. A.; Chen, H.-W. J Am Chem Soc 1979, 101, 390.

[7] (a) Ando, W.; Hanyu, Y.; Takata, T. J Am Chem Soc 1982, 104, 4981; (b) Ando, W.; Hanyu, Y.; Takata, T.; Sakurai, T.; Kobayashi, K. Tetrahedron Lett 1984, 25, 1483; (c) Ando, W.; Hanyu, Y.; Takata, T. J Org Chem 1986, 51, 2122.

[8] Köpke, B.; Voss, J. J Chem Res, Synop 1982, 314.

[9] Capozzi, G.; Romeo, G.; Marcuzzi, F. J Chem Soc, Chem Commun 1982, 959.

[10] Lucchini, V.; Modena, G.; Pasquato, L. J Am Chem Soc 1991, 113, 6600.

[11] Criegee, R.; Moschel, A. Chem Ber 1959, 92, 2181.