Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Rearrangement of the *tert*-butyl group of 5,6-di-*tert*-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide

Sanae Yoshida[a]; Yuta Morohashi[a]; Takashi Fujihara[a]; Yoshiaki Sugihara[a]; Juzo Nakayama[a]
[a] Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Sakura-ku, Saitama, Japan

To cite this Article Yoshida, Sanae , Morohashi, Yuta , Fujihara, Takashi , Sugihara, Yoshiaki and Nakayama, Juzo(2008) 'Rearrangement of the *tert*-butyl group of 5,6-di-*tert*-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide', Journal of Sulfur Chemistry, 29: 1, 1 — 7
To link to this Article: DOI: 10.1080/17415990701753373
URL: http://dx.doi.org/10.1080/17415990701753373

Journal of Sulfur Chemistry
Vol. 29, No. 1, February 2008, 1–7

Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

Rearrangement of the *tert*-butyl group of 5,6-di-*tert*-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide

Sanae Yoshida, Yuta Morohashi, Takashi Fujihara, Yoshiaki Sugihara and Juzo Nakayama*

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Sakura-ku, Saitama, Japan

(*Received 22 August 2007; final version received 11 October 2007*)

Treatment of 5,6-di-*tert*-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide with trimethylsilyl trifluoromethanesulfonate at room temperature resulted in the rearrangement of *tert*-butyl group to furnish 4,6-di-*tert*-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide quantitatively. Meanwhile, treatment of the compound by trimethyloxonium tetrafluoroborate afforded 4,5-di-*tert*-butyl-1,2-dithiin 1,1-dioxide in addition to the above rearrangement product.

Keywords: rearrangement; 2,3,7-trithiabicylo-5-ene 7-oxide; 1,2-dithiin; trimethylsilyl trifluoromethanesulfonate; trimethyloxonium tetrafluoroborate

1. Introduction

We have been investigating small molecules of sulfur such as diatomic sulfur (S_2), sulfur monoxide (SO) (*1*), disulfur monoxide (S=S=O) (*2–5*), and triatomic sulfur (S=S=S) (*5*). We thus reported that compound **2**, which is easily obtainable by oxidation of **1** with dimethyldioxirane, undergoes a retro-Diels–Alder reaction to give thiophene 1-oxide **3** and S=S=O (*5*). In this connection, we have now investigated the Pummerer reaction of **1** with expectation that if the Pummerer product **4** formed, it would undergo a retro-Diels–Alder reaction to generate singlet diatomic sulfur ($^1S_2$). Incidentally, **1** is thermally stable and does not show any tendency to undergo a retro-Diels–Alder reaction to generate S_2 (*5*). During this study, we have now found that treatment of **1** with trimethylsilyl trifluoromethanesulfonate ($CF_3SO_3SiMe_3$) results in the rearrangement of *tert*-butyl group to give **6** (Scheme 1).

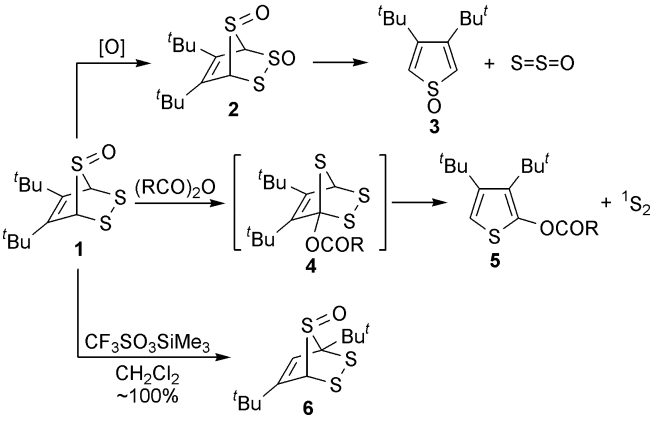
2. Results and discussion

Initially, we have treated **1** with $(CH_3CO)_2O$ or with $(CF_3CO)_2O$ in CH_2Cl_2 or without the solvent at room temperature, but no reaction took place. The reaction, carried out under more

*Corresponding author. Email: nakayama@mail.saitama-u.ac.jp

ISSN 1741-5993 print/ISSN 1741-6000 online

DOI: 10.1080/17415990701753373
http://www.informaworld.com



Scheme 1.

forcing conditions, gave intractable mixtures. Then, **1** was treated with a stronger electrophile, $CF_3SO_3SiMe_3$. Thus treatment of **1** with one molar equivalent of this reagent produced **6** in 92% yield with recovery of **1** in 6% at room temperature, whereas the use of 0.1 molar equivalent of the reagent gave **6** only in a low yield (91:9 mixture of 1 and 6). On the other hand, the use of ten molar equivalents gave **6** quantitatively. Although the ^{1}H and ^{13}C NMR spectral data revealed that **6** has a partial structure of $-C(^tBu)=CH-CH(^tBu)-$, we could not determine its structure unequivocally, including the stereochemistry of the S=O group, the existence of which was suggested by the IR spectrum. Thus, the structure elucidation was done by X-ray diffraction analysis. Figure 1 shows the molecular structure of **6** in which the stereochemistry of the S=O group of **l** is retained. The relevant structural data of **6** are summarized in Table 1.

Next, reactions of **1** with $BF_3 \bullet Et_2O$ and $Me_3O^+BF_4^-$ were examined to know more about the rearrangement. The reaction with $BF_3 \bullet Et_2O$ proceeded slowly at room temperature to give **6** in 31% yield with recovery of **1** in 64% after 5 days and the reaction in refluxing $CHCl_3$ gave **6** in 83% yield with recovery of **1** in 10% after 24 h. On the other hand, treatment of **1** with $Me_3O^+BF_4^-$ at room temperature gave **6**, 4,5-di-*tert*-butyl-1,2-dithiin 1,1-dioxide (**7**), and 3,4-di-*tert*-butylthiophene (**8**) in 11%, 19%, and 31% yields, respectively, with recovery of **1** in 27%. The vinyl protons of **7** appeared as singlet at δ 6.96 and 7.17 in the ^{1}H NMR and the two sp^2 carbons carrying *tert*-butyl group appeared at characteristic low fields of δ 152.0 and 160.8 in the ^{13}C NMR, and the IR spectrum showed asymmetric and symmetric absorptions of the SO_2 group at 1316 and 1134 cm^{-1}, respectively (Scheme 2).

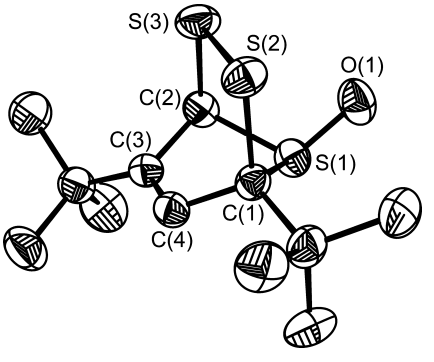
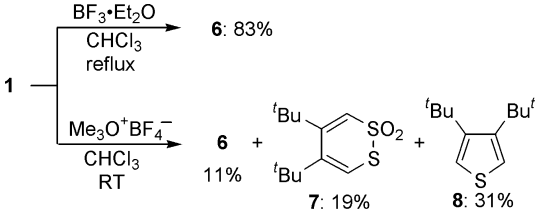


Figure 1. ORTET plot of molecular structure of **6**.

Table 1. Selected bond lengths, bond angles, and dihedral angles from the X-ray structure of **6**.

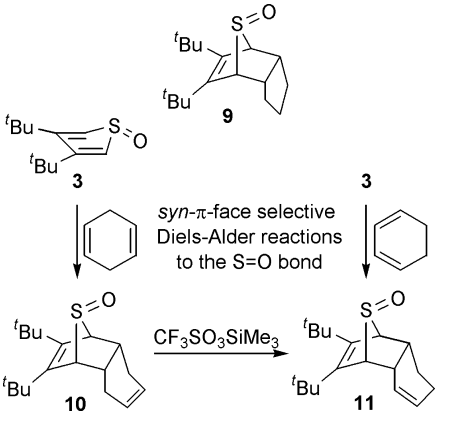
Bond lengths [Å] and angles [°] for **6**	
C(1)-C(4) 1.484(3)	C(4)-C(1)-S(2) 109.99(14)
C(1)-S(2) 1.853(2)	C(4)-C(1)-S(1) 98.01(13)
C(1)-S(1) 1.873(2)	S(2)-C(1)-S(1) 104.69(10)
C(2)-C(3) 1.494(3)	C(3)-C(2)-S(3) 111.92(15)
C(2)-S(3) 1.824(2)	C(3)-C(2)-S(1) 100.28(14)
C(2)-S(1) 1.832(2)	S(3)-C(2)-S(1) 107.14(11)
C(3)-C(4) 1.329(3)	C(4)-C(3)-C(2) 109.66(19)
O(1)-S(1) 1.4803(18)	C(3)-C(4)-C(1) 115.04(19)
S(2)-S(3) 2.0676(8)	O(1)-S(1)-C(2) 110.89(10)
	O(1)-S(1)-C(1) 111.60(10)
	C(2)-S(1)-C(1) 83.26(9)
	C(1)-S(2)-S(3) 96.46(7)
	C(2)-S(3)-S(2) 95.82(7)
Dihedral angles [°] for **6**	
S(3)-C(2)-C(3)-C(4) −73.7(2)	C(4)-C(1)-S(1)-O(1) 157.35(13)
S(1)-C(2)-C(3)-C(4) 39.7(2)	S(2)-C(1)-S(1)-O(1) 44.16(13)
C(2)-C(3)-C(4)-C(1) −2.1(3)	C(4)-C(1)-S(1)-C(2) 47.51(14)
S(2)-C(1)-C(4)-C(3) 73.7(2)	S(2)-C(1)-S(1)-C(2) −65.69(10)
S(1)-C(1)-C(4)-C(3) −35.2(2)	C(4)-C(1)-S(2)-S(3) −61.03(14)
C(3)-C(2)-S(1)-O(1) −160.65(14)	S(1)-C(1)-S(2)-S(3) 43.38(9)
S(3)-C(2)-S(1)-O(1) −43.72(14)	C(3)-C(2)-S(3)-S(2) 65.38(15)
C(3)-C(2)-S(1)-C(1) −50.06(14)	S(1)-C(2)-S(3)-S(2) −43.61(10)
S(3)-C(2)-S(1)-C(1) 66.88(11)	C(1)-S(2)-S(3)-C(2) −0.86(10)



Scheme 2.

Next, we have synthesized compounds **9** and **10**, and examined the reaction with $CF_3SO_3SiMe_3$. It is well documented that Diels–Alder reactions of **3** takes place exclusively at the *syn*-π-face to the S=O bond (*6*, *7*). Thus, compounds **9** (*7*) and **10** were prepared by Diels–Alder reactions of **3** with cyclopentene and 1,4-cyclohexadiene, respectively. However, compound **9** did not undergo any reaction even when heated with a large excess of $CF_3SO_3SiMe_3$ in refluxing $CHCl_3$. Meanwhile, heating **10** with a large excess of $CF_3SO_3SiMe_3$ in refluxing 1,2-dichloroethane for 5 days resulted in the migration of the double bond to provide a mixture of **11** and **10** in the ratio 96:4. No rearrangement of the *tert*-butyl group was observed. The structure of **11** was determined by independent synthesis: the Diels–Alder reaction of **3** with 1,3-cylohexadiene gave **11** in 91% yield. CF_3SO_3H, even if existed in the reaction mixture as impurity, would not be involved in the above isomerization because **11** was not formed when **10** was heated with CF_3SO_3H in $CDCl_3$ in a sealed NMR tube at 70 °C for 4 days. DFT calculations predicted that **11** is a more stable isomer than **10** by 3.34 kcal/mol (B3LYP/6-31G** level) (*8*) (Scheme 3).

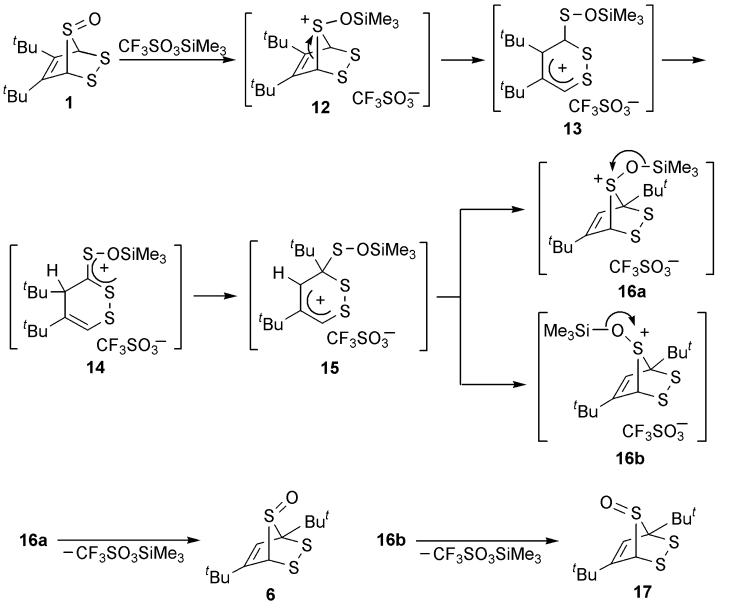
The following mechanism is proposed for the isomerization of **1** to **6**. A hard electrophile $CF_3SO_3SiMe_3$ initially reacts with the oxygen atom of the S=O to give sulfonium ion intermediate **12**, which undergoes ring-opening to produce carbonium ion **13** stabilized by the double



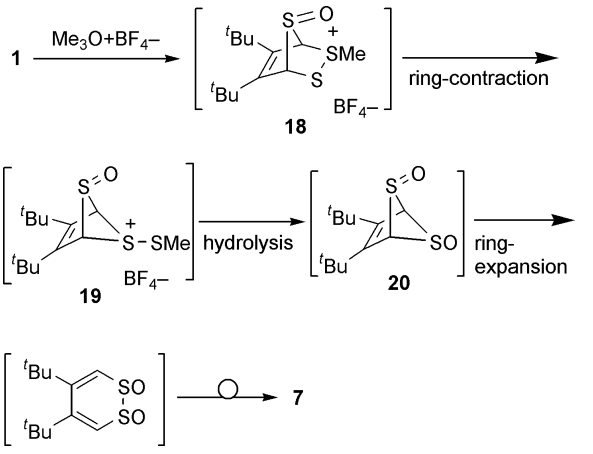
Scheme 3.

bond and the sulfur atom. Since **9** and **10** do not undergo the rearrangement of the *tert*-group, stabilization by the sulfur atom would be crucial to the ring-opening of **12**. Then the position exchange takes place between hydrogen and *tert*-butyl group to afford another carbonium ion **15** via **14**. DFT calculations predicted that **16a** is more stable than **16b** by 6.4 kcal/mol. Thus, cyclization of **15** produces more stable **16a** selectively. Finally elimination of $CF_3SO_3SiMe_3$ from **16a** would complete the isomerization to **6**. If this mechanism is operative, a catalytic amount of $CF_3SO_3SiMe_3$ could cause the complete isomerization of **1** to **6**, even though the conversion is slow. However, for example, the use of 0.1 molar amount of $CF_3SO_3SiMe_3$ produced **6** only in 9% yield. This is the weak point of this mechanism (Scheme 4).

As to the formation of **7**, the following is proposed tentatively. $Me_3O^+BF_4^-$ is a softer nucleophile than $CF_3SO_3SiMe_3$. Thus it undergoes competitive methylation of the oxygen and sulfur



Scheme 4.



Scheme 5.

atoms to produce **12** and **18**, respectively. Then **18** undergoes a series of reactions, shown in Scheme 5, to give **7** (*9*). Hydrolysis of **19** to **20** may occur during work-up procedure.

3. Experimental

3.1. *Rearrangement of 5,6-di-tert-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide (1) to 4,6-di-tert-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide (6) by $CF_3SO_3SiMe_3$*

A mixture of **1** (200 mg, 0.72 mmol) and $CF_3SO_3SiMe_3$ (161 mg, 0.72 mmol) in $CHCl_3$ (16 mL) was stirred at room temperature for 2 days. The reaction was quenched by addition of iced-water, washed with aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. The $CHCl_3$ was evaporated and the residue was subjected to silica gel column chromatography. Elution of the column with hexane:AcOEt (3:1) gave **6** (184 mg, 92%) and then **1** (11 mg, 6%).

The reaction, carried out by using 10 molar equivalents of $CF_3SO_3SiMe_3$at room temperature for one day, gave **6** quantitatively. On the other hand, the reaction, carried out by using 0.1 molar equivalent of $CF_3SO_3SiMe_3$at room temperature for 3 days, gave a 91:9 mixture of **1** and **6**.

6. Yellow crystals (from Et_2O). Mp: 144.5–145 °C (dec.). IR (KBr): 1065 cm^{-1} (S=O). ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 9H), 1.33 (s, 9H), 5.12 (d, $J = 1.1$ Hz, 1H), 5.79 (d, $J = 1.1$ Hz, 1H). ^{13}C NMR (100.5 MHz, $CDCl_3$): 29.20, 29.35, 33.85, 35.75, 75.67, 104.59, 119.48, 146.54. MS (EI, 70 eV): m/z 286 (M^+). UV (CH_3CN) λ_{max} (ε): 281 (570), 346 nm (37, sh). Anal. Calcd. for $C_{12}H_{30}OS_3$: C, 52.13; H, 7.29. Found: C, 52.23; H, 7.29.

3.2. *Rearrangement of 5,6-di-tert-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide (1) to 6-di-tert-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide (6) by $BF_3 \bullet Et_2O$*

A mixture of **1** (50 mg, 0.18 mmol) and $BF_3 \bullet Et_2O$ (46 μL, 0.37 mmol) in $CHCl_3$ (4 mL) was stirred at room temperature for 5 days to give **6** (15 mg, 31%) and the starting material (32 mg, 64%). On the other hand, heating a mixture of **1** (50 mg, 0.18 mmol) and $BF_3 \bullet Et_2O$ (46 μL, 0.37 mmol) in $CHCl_3$ (4 mL) at reflux for one day gave 42 mg (83%) of **6** and the starting material (5 mg, 10%).

3.3. *Reaction of 5,6-di-tert-butyl-2,3,7-trithiabicylo-5-ene 7-endoxide (1) by trimethyloxonium tetrafluroborate*

A mixture of **1** (50 mg, 0.18 mmol) and $Me_3O^+BF_4^-$ (32 mg, 0.21 mmol) in $CHCl_3$ (4 mL) was stirred at room temperature for 4 days. The reaction mixture was purified by silica gel column chromatography to give 11 mg (31%) of 3,4-di-*tert*-butylthiophene (**8**), 9 mg (19%) of 4,5-di-*tert*-butyl-1,2-dithiin 1,1-dioxide (**7**), 5 mg (11%) of **6**, and 14 mg (27%) of the starting material.

7. Colorless needles (from pentane). Mp: 74.5–75.5 °C. IR (KBr): 1316, 1134 cm^{-1} (SO_2). ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 9H), 1.36 (s, 9H), 6.96 (s, 1H), 7.17 (s 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 31.51, 32.09, 38.24, 38.72, 115.77, 137.45, 152.06, 160.80. MS (EI, 70 eV): m/z 260 (M^+). Anal. Calcd for $C_{12}H_{20}O_2S_2$: C, 55.34; H, 7.74. Found: C, 55.48; H, 7.70.

3.4. *Preparation of 10 by Diels–Alder reaction of 3 with 1,4-cyclohexadiene*

Thiophene 1-oxide **3** (213 mg, 1 mmol) and 1,4-cyclohexadiene (3 mL, 32 mmol) were heated at 100 °C in a sealed tube for 18 h. The excess diene was evaporated and the residue was purified by silica gel column chromatography to give 145 mg (50%) of **10**. Colorless plates (from hexane). Mp: 148.0–148.5 °C. IR (KBr): 1074 cm^{-1} (S=O). ^1H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 18H), 1.85–1.91 (m, 2H), 2.31–2.34 (m, 2H), 2.95–2.98 (m, 2H), 3.89 (broad t, $J = 1.7$ Hz, 2H), 5.92–5.94 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 26.32, 32.57, 34.26, 35.86, 69.41, 128.89, 142.92. MS (EI, 70 eV): m/z 292 (M^+). Anal. Calcd for $C_{18}H_{28}OS$: C, 73.92; H, 9.65. Found: C, 73.75; H, 9.74.

3.5. *Rearrangement of 10 to 11 by $CF_3SO_3SiMe_3$*

A mixture of **10** (29 mg, 0.1 mmol) and $CF_3SO_3SiMe_3$ (0.18 mL, 1 mmol) in 1,2-dichloroethane (5 mL) was heated at reflux for 5 days. The reaction gave a 96:4 mixture of **11** and **10**. Compound **11** could not be isolated in pure form despite many efforts. Thus, the authentic sample of **11** was obtained by alternative synthesis. The reaction, carried out by using one molar equivalent of $CF_3SO_3SiMe_3$ at room temperature for 5 days, resulted in the quantitative recovery of **10**, and the reaction, carried out in refluxing $CHCl_3$ for 5.5 h by using two molar equivalents of $CF_3SO_3SiMe_3$ gave a 37:63 mixture of **11** and **10**.

3.6. *Preparation of 11 by Diels–Alder reaction of 3 with 1,3–cyclohexadiene*

Thiophene 1-oxide **3** (50 mg, 0.24 mmol) and 1,3-cyclohexadiene (1.5 mL, 16 mmol) were heated at 100 °C in a sealed tube for 3 days. The excess diene was evaporated and the residue was purified by silica gel column chromatography to give 64 mg (91%). Colorless plates (from cyclohexane). Mp: 146.5–147.5 °C. IR (KBr): 1073 cm^{-1} (S=O). ^1H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9H), 1.25 (s, 9H), 1.22–1.25 (m, 1H), 1.81–1.88 (m, 1H), 1.97–1.99 (m, 2H), 2.91–2.98 (m, 1H), 3.27 (broad d, $J = 9.9$ Hz, 1H), 3.96 (s, 1H), 3.97 (s, 1H), 5.78 (broad d, $J = 9.9$ Hz, 1H), 5.92–5.98 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 23.78, 24.12, 32.46, 32.65, 33.18, 33.68, 33.96, 34.24, 69.41, 69.91, 127.34, 130.10, 142.11, 142.57. MS (EI, 70 eV): m/z 292 (M^+). Anal. Calcd for $C_{18}H_{28}OS$: C, 73.92; H, 9.65. Found: C, 74.06; H, 9.73.

3.7. *X-Ray crystallographic analysis data of 6*

Crystal data for **6** were recorded on a Bruker SMART APEX CCD area detector by using 0.30°-wide ω scans and graphite-monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). Frame

data (20 s, 0.30°-wide ω scans) were collected using the Bruker SMART software package. Peak integration was performed by the Bruker SAINT-Plus software package. Absorption correction was made by the software SADABS. Space group determination was done by the software XPREP. All calculations were performed by the Bruker SHELXTL 5.1 software package. The structure was solved by direct methods and refined with full-matrix least-squares by all independent reflections. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions. **6**: C12H20OS3, M = 276.46, tetragonal, space group P-42(1)c; a = 17.0735(5), b = 17.0735(5), c = 9.8863(4) Å; Z = 8; V = 2881.90(17) Å^3, Dc = 1.274 g/cm^3, μ = 0.494 mm^{-1}; measured reflections 20734, independent reflections 3449 [R(int) = 0.0425], R = 0.0409, Rw = 0.0919, GOF = 1.083. (Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 656812 for **6**. Copies of this information can be obtained from The Director, DDCD, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).)

References

(1) Nakayama, J.; Tajima, Y.; Piao, X.-H.; Sugihara, Y. *J. Am. Chem. Soc.* **2007,** *129,* 7250.
(2) Ishii, A.; Nakabayashi, M.; Nakayama, J. *J. Am. Chem. Soc.* **1999,** *121,* 7959.
(3) Ishii, A.; Nakabayashi, M.; Jin, Y.-N.; Nakayama, J. *Organomet. Chem.* **2000,** *611,* 127.
(4) Ishii, A.; Kawai, T.; Tekura, K.; Oshida, H.; Nakayama, J. *Angew. Chem., Int. Ed.* **2001,** *40,* 1924.
(5) Nakayama, J.; Aoki, S.; Takayama, J.; Sakamoto, A.; Sugihara, Y.; Ishii, A. *J. Am. Chem. Soc.* **2004,** *126,* 9085.
(6) Otani, T.; Takayama, J.; Suighara, Y.; Ishii, A.; Nakayama, J. *J. Am. Chem. Soc.* **2003,** *125,* 8255.
(7) Takayama, J.; Sugihara, Y.; Takayanagi, T.; Nakayama, J. *Tetrahedron Lett.* **2005,** *46,* 4165.
(8) Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery Jr, J.A.; Vreven, T.; Kudin, K.N.; Burant, J.C *et al.*, Pople, J. A. Gaussian 03, Revision B. 05; Gaussian: Wallingford CT, 2004.
(9) For *vic*-disulfoxide, see Ishii, A.; Nakabayashi, M.; Nakayama, J. *J. Am. Chem. Soc.* **1999,** *121,* 7959 and references cited therein.