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Headline Articles

First Synthesis and Reactivities of Isolable Dithiiranes and Their 1-Oxides

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The reaction of the 6-*exo*-oxide of 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane (**2**) with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ gave the first isolable dithiirane oxide, (1*RS*, 3*SR*)-3-phenyl-3-(1,1,3,3-tetramethyl-4-oxo-4-phenylbutyl)dithiirane 1-oxide (**1**), while the 6-*endo*-oxide of **2** gave both **1** and its (1*RS*, 3*RS*)-isomer **10**. Under similar reaction conditions, **2** yielded the first isolable, unoxidized dithiirane, 3-phenyl-3-(1,1,3,3-tetramethyl-4-oxo-4-phenylbutyl)dithiirane (**3**). The dithiirane **3** was also obtained by treatment of **2** with NaOCl–$NaClO_4$. The X-ray structure analyses were performed for **1**, **3**, and **10**. Treatment of unsymmetrical 8,8-dimethyl-1,9-diphenyl-10,11-dithiatricyclo[7.1.1.$0^{2,7}$]-undeca-2,4,6-triene with NaOCl–$NaClO_4$ gave 3-[1-(*o*-benzoylphenyl)-1-methylethyl]-3-phenyldithiirane selectively in good yield. However, 1,3-dithietanes, prepared from adamantane-2-thiones, failed to give the corresponding dithiiranes by treatment with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ or NaOCl–$NaClO_4$. The dithiirane **3** thermally isomerized to 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-6,7-dithiabicyclo[3.2.1]octane probably via 2,2,4,4-tetramethyl-1,5-diphenyl-5-thioxo-1-pentanone *S*-sulfide.

Dithiiranes are the smallest cyclic disulfides (Chart 1). In dithiiranes, the dihedral angle of 0° leads to significant repulsive interactions between lone pair electrons on sulfur atoms in addition to large angle strains.[1] Therefore, although several dithiiranes have been recognized as elusive intermediates, no isolable examples including their oxidized derivatives were reported in spite of much effort[2] until our preliminary reports on the first isolable dithiirane oxide **1** had appeared.[3] Dithiiranes are also of interest as isomers of thioketone *S*-sulfides and dithioesters.[2,4] Meanwhile, dioxiranes (oxygen analog) are known and used as oxidizing reagents, though they are not very stable molecules.[5]

We had investigated the preparation and reactions of bicyclic 1,3-dichalcogenetanes and also of sulfur and selenium analogs of bicyclic ozonides.[6] During the course of the oxidation study of these bicyclic compounds,[7] we serendipitously found that the oxides of the 6,7-dithiabicyclo[3.1.1]-heptane (bicyclic 1,3-dithietane) **2** led to the formation of the first isolable dithiirane oxide derivative **1** by treatment with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (OXONE®) in dichloromethane–water in the presence of a phase-transfer catalyst (Chart 2).[3] Taking advantage of this finding, we further succeeded in the preparation of the isolable, unoxidized dithiirane derivative **3**.[8] In this paper, we fully report the synthesis of the isolable dithiiranes from the bicyclic 1,3-dithietanes under oxidative hydrolysis conditions.[9] The scope and limitations of this synthetic method[10] and structures and some

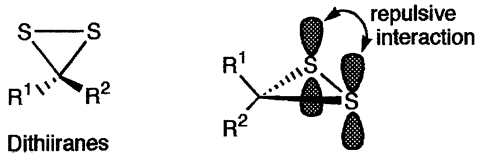


Chart 1.

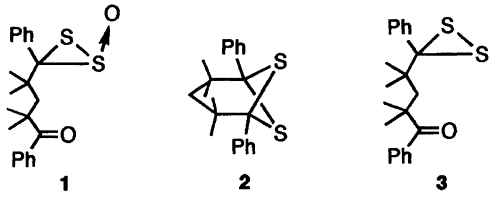
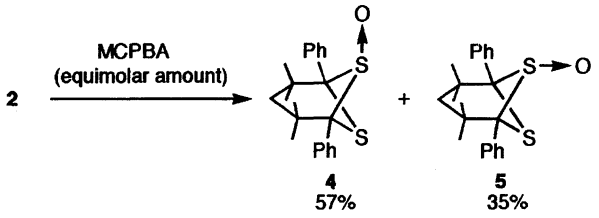


Chart 2.

chemical properties of the dithiiranes are also discussed.

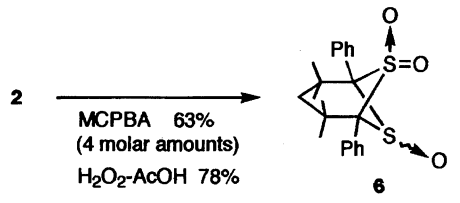
Results and Discussion

Isolation of the First Isolable Dithiirane Oxide. Oxidation of **2**[6] with *m*-chloroperbenzoic acid (MCPBA) afforded *endo*- and *exo*-sulfoxides **4** and **5** in 57 and 35% yields (Eq. 1), respectively.



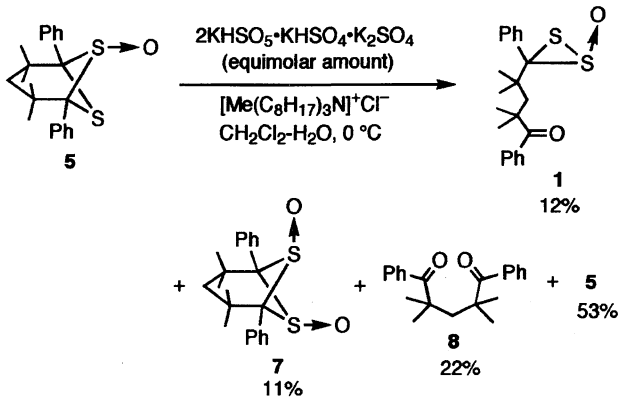
(1)

The oxidation of **2** with 4 molar amounts of MCPBA or H_2O_2–AcOH gave *S,S,S'*-trioxide **6** in 63 or 78% yield (Eq. 2), respectively.



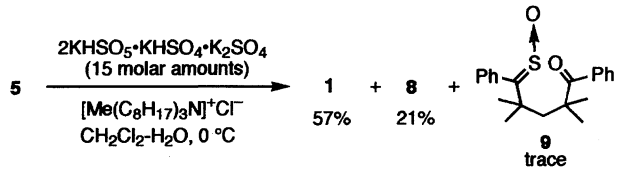
(2)

The stereochemistry of the two isomeric sulfoxides was elucidated by ^{1}H NMR study using Eu(fod)$_3$ as the shift reagent (see Experimental). When further oxidation of the *exo*-sulfoxide **5** was carried out with an equimolar amount of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$[11] in the presence of a small amount of $[Me(C_8H_{17})_3N]^+Cl^-$ in CH_2Cl_2–H_2O at room temperature, we obtained an unknown compound (12% yield as **1**) along with *S-endo*, *S'-exo*-*S,S'*-dioxide **7** (11%), dicarbonyl compound **8**[12] (22%), and the starting material **5** (53%) (Eq. 3).



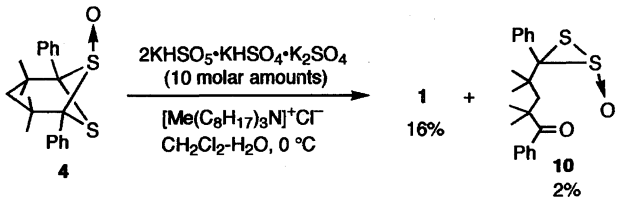
(3)

The ^{1}H and ^{13}C NMR spectra showed that the unknown compound contains four methyl groups, two phenyl groups, which are chemically nonequivalent, in addition to one methylene and one carbonyl group. Furthermore, the IR spectrum showed absorptions due to carbonyl (1673 cm^{-1}) and sulfinyl (1142 cm^{-1}) groups. We have therefore given a dithiirane oxide structure **1** to this compound, based on these spectroscopic data and a result of elemental analysis. However, the formation of **1** was such an unexpected and unbelievable result that the compound was subjected to X-ray single crystal structure analysis. An ORTEP structure of **1** can be given in Fig. 1. After some effort, we have found that the dithiirane oxide **1** is obtained in an optimized yield of 57%, along with a trace amount of the thioketone *S*-oxide **9** and the dicarbonyl compound **8** (21%), when the *exo*-sulfoxide **5** was treated with excess $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (15 molar amounts) in the presence of $[Me(C_8H_{17})_3N]^+Cl^-$ in CH_2Cl_2–H_2O at 0 °C (pH3—6) (Eq. 4).



(4)

On the other hand, treatment of the *endo*-sulfoxide **4** with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ at room temperature also gave the (1*RS*, 3*SR*)-dithiirane 1-oxide **1** in 26% yield along with **8** (52%) under the pH-controlled conditions. Interestingly, the reaction, conducted at lower temperature (0 °C), yielded the (1*RS*, 3*RS*)-dithiirane 1-oxide **10**, though in a low yield (2%), in addition to **1** (16%) (Eq. 5). The structure of this (1*RS*, 3*RS*)-isomer was confirmed by the spectroscopic data and X-ray structure analysis (Fig. 2).



(5)

The formation of the dithiirane oxides **1** and **10** can be formulated tentatively, as shown in Scheme 1. Since the present reaction did not proceed under neutral or alkaline

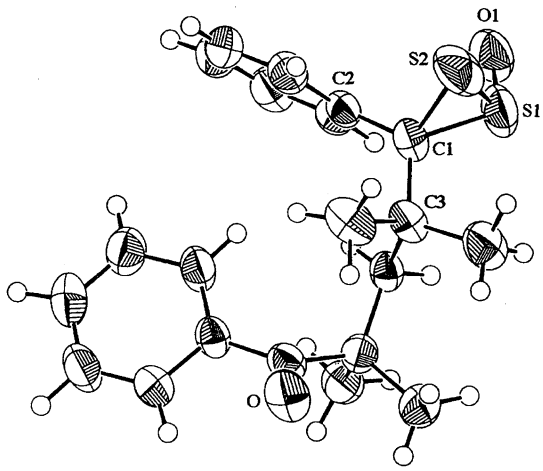


Fig. 1. An ORTEP view of the (1*RS*, 3*SR*)-dithiirane 1-oxide **1**.

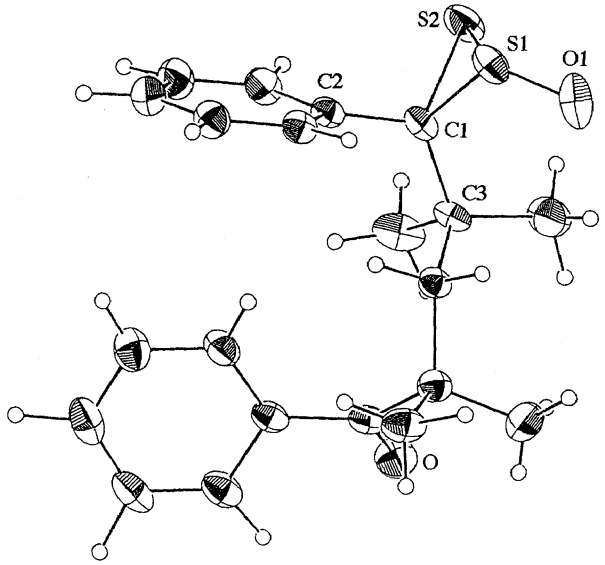


Fig. 2. An ORTEP view of the (1*RS*, 3*RS*)-dithiirane 1-oxide **10**.

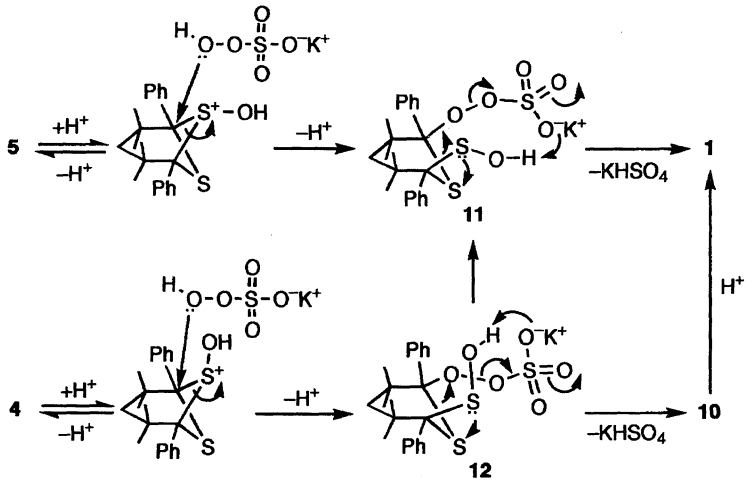
conditions, protonation on the sulfoxide oxygen of **5** should take place first to assist a nucleophilic attack of $KHSO_5$ on the bridgehead carbon. This is followed by ring opening to give a sulfenic acid intermediate **11**. The ring opening may be an S_N1 process involving a carbocation intermediate stabilized by the phenyl group and the sulfur atom.[5b,5c] Then, the intramolecular cyclization of **11** would give rise to **1** exclusively in a stereospecific manner, if it takes place quickly. In the case of **4**, the cyclization of a sulfenic acid **12** is slow enough to allow conformation change to the rotamer **11**, which results in the formation of **1** exclusively or the formation of a mixture of **1** and **10**, depending on the reaction temperature.

The (1*RS*, 3*SR*)-dithiirane 1-oxide **1** is a rather thermally stable, crystalline compound, mp 124—125 °C (decomp), while the (1*RS*, 3*RS*)-isomer **10** is susceptible to isomerization to **1** or decomposition to **8** during chromatographic purification. The ORTEP drawing structures of **1** and **10** were given in Figs. 1 and 2 and the relevant bond lengths and angles data are listed in Table 1. In the X-ray structure analysis of **1**, disorder of the position of the sulfoxide oxygen is observed, that is, probabilities of observing the oxygen on S1 and S2 are 80 and 20%, respectively. In these circumstances, the observed bond distances of two C–S bonds of **1** [1.833(4) and 1.830(4) Å] are virtually equal and these bond distance values, including the S–S bond distance [2.074(2) Å], are very similar to the calculated bond distances of the parent dithiirane (HF/3-21G(*): C–S: 1.793 Å; S–S: 2.072 Å).[1b] Disorder of the position of the sulfoxide oxygen is also observed in the (1*RS*, 3*RS*)-isomer **10** and probabilities of observing the oxygen on S1 and S2 are 83 and 17%, respectively. The S–S bond length [2.107(2) Å] is slightly longer than that of **1**, while the C–S bond lengths [1.832(5) Å] are quite similar to those of **1**.

Preparation of Unoxidized Dithiiranes. Taking advantage of the first isolation of dithiirane oxides, our attention was directed to the preparation of unoxidized dithiiranes.

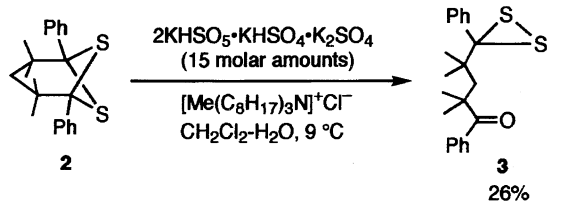
Table 1. Relevant Bond Lengths (Å) and Angles (°) Data of (1*RS*, 3*SR*)-Dithiirane 1-Oxide **1**, (1*RS*, 3*RS*)-Dithiirane 1-Oxide **10**, and Dithiirane **3**

	1	**10**	**3**
C1–S1	1.833(4)	1.832(5)	1.821(2)
C1–S2	1.830(4)	1.832(5)	1.814(3)
C1–C2	1.499(5)	1.490(7)	1.515(3)
C1–C3	1.568(5)	1.575(7)	1.566(3)
S1–S2	2.074(2)	2.107(2)	2.073(2)
S1–O1	1.442(4)	1.415(5)	—
C1–S1–S2	55.5(1)	54.9(2)	55.07(8)
S1–S2–C1	55.6(1)	54.9(2)	55.37(8)
S1–C1–S2	69.0(1)	70.2(2)	69.55(9)
C2–C1–C3	118.3(3)	117.9(4)	117.2(2)
S2–C1–C2	113.7(3)	112.6(4)	113.3(2)
S2–C1–C3	116.4(3)	117.5(4)	118.0(2)
S1–C1–C2	113.8(3)	110.4(4)	113.1(2)
S1–C1–C3	116.2(3)	119.4(4)	117.0(2)
S2–S1–O1	111.2(2)	115.5(3)	—
C1–S1–O1	113.9(2)	116.7(3)	—



Scheme 1.

We then thought that treatment of unoxidized bicyclic 1,3-dithietane **2** with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ would give the corresponding unoxidized dithiirane. Thus, a CH_2Cl_2 solution of **2**, an aqueous solution of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, and a catalytic amount of $[Me(C_8H_{17})_3N]^+Cl^-$ were mixed up and stirred vigorously in a refrigerator (at ca. 9 °C) for 4 d (pH5—7). The color of the CH_2Cl_2 layer of the mixture gradually turned from colorless to yellow. After the careful evaporation of the organic layer, the residue was dissolved in CH_2Cl_2 and the solution diluted with hexane. The resulting mixture was allowed to stand in a refrigerator and the first white crystalline crop, which consisted of by-products, was removed by filtration. The filtrate was cooled again in the refrigerator for 2 d to separate orange crystals. Purification of the crystals with medium-pressure liquid chromatography (MPLC) provided the desired dithiirane **3** in 26% yield (Eq. 6).



(6)

The dithiirane **3** is an orange crystalline compound that is stable at room temperature under air but, when heated at 68—75 °C in a capillary tube, decomposed to give the thioketone **13**[13] and elemental sulfur (Chart 3). The structure of **3** was determined by spectroscopic means and X-ray structure analysis (Fig. 3). In the UV-vis spectrum, the longest absorption maximum (λ_{max}) was observed at 452 nm (ε 104). This absorption corresponds to the first transition ($n_\pi \rightarrow$S–S, S–C σ^*, 422 nm) of the parent dithiirane calculated by Snyder and Carlsen with the CNDO/S-CI method.[1a] As to the X-ray structure of **3**, no remarkably unusual bond lengths and angles were observed in the dithiirane ring (Table 1). The observed S–S bond length, 2.073(2) Å, corresponds to the mean value (2.070 Å)[14] of S–S bond lengths of disulfides in which the dihedral angles between two C–S bonds are constrained to 0—20°, and the two C–S bond distances (1.821(2) and 1.814(3) Å) are very similar to that of the parent thiirane (1.815 Å).[15]

The reaction of **2** with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ giving **3** corresponds to an oxidative hydrolysis of a dithioacetal.[16] In our case, the two sulfur atoms of **2** remain in the same molecule by forming a disulfide bond. From this standpoint of view, we examined the reaction of **2** with some oxidants under hydrolytic conditions to find other methods for the preparation of dithiiranes.

The dithiirane **3** is so unstable under basic conditions

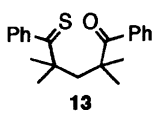


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Chart 3.

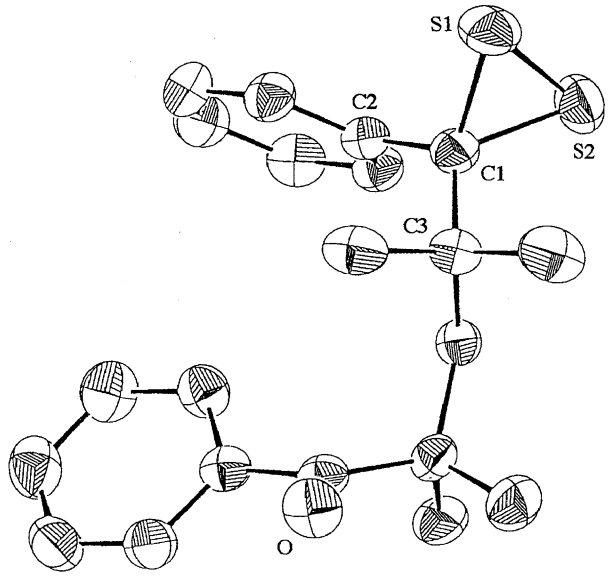


Fig. 3. An ORTEP view of the dithiirane **3**.

that oxidative hydrolysis of **2** must be carried out under neutral to acidic conditions. After a survey of several combinations of an oxidant and an acid such as MCPBA–CF_3CO_2H,[17] H_2O_2–HCl,[18] CF_3CO_2H–H_2O_2, $KHSO_4$–H_2O_2, and BF_3–PbO_2,[16c] we found that the reaction of **2** with H_2O_2–HCl in CH_2Cl_2–H_2O at room temperature yielded the dithiirane **3** in 11% (UV-vis) (Table 2, Run 1). Thus, or attention was focused on the reagents which generate positive halogen species such as hypochlorous acid (HOCl) and sodium hypochlorite (NaOCl). In the case of HOCl (at room temperature),[19] the colorless organic layer quickly turned yellow, which is indicative of the formation of **3**. After 7 min, an analysis of the organic layer by UV-vis spectroscopy revealed the formation of **3** in 18% yield. However, the ^1H NMR spectrum of the mixture indicated the formation of a 6-oxa-7,8-dithiabicyclo[3.2.1]octane derivative **14**[20] as the main product (Run 2) (Chart 4). On the other hand, vigorous stirring of a solution of **2** in CH_2Cl_2 with aqueous NaOCl[21] at 0 °C gave **3** as the main product (ca. 50%) (Runs 4 and 5). Moreover, a special effect due to $LiClO_4$[22] was observed; addition of $LiClO_4$ (1.4 molar amount) provided a remarkable reduction in the reaction time as well as a decrease of the yields of by-products (Run 6). Results of the reactions using $NaClO_4$ and LiCl as an additive (Runs 7 and 9) clearly show that perchlorate ion plays an important role in increasing the yield of **3**. In Run 8, as high as a 48% isolated yield of **3** could be obtained in pure form by purification with MPLC. In a similar manner, dithiiranes **15** and **16** were synthesized from the corresponding bicyclic 1,3-dithietanes **17** and **18**, respectively, as yellow to orange crystalline materials in 39 and 37% yields, respectively.

We previously reported that isomerization of the *endo*-sulfoxide **4** to the 6-oxa-7,8-dithiabicyclo[3.2.1]octane **14** is mediated by an acidic cray.[20] In the present case, however, the reaction of the sulfoxide **4** with HOCl for 7 min gave no **14** in any amount, and instead gave a mixture of (1*RS*,

Table 2. Reaction of **2** with H_2O_2–HCl, HOCl, and NaOCl

Run	Reagent (mol amount)	Additive	Time h	Products/Yields(%)[a] 3	1	14	4	8	2
1	H_2O_2–HCl (9)	—	120	11[b]	c)	c)	c)	c)	c)
2	HOCl (min 0.9)	—	0.1	18[b]	0	46	18	1	0
3	NaOCl (0.84)	—	4	41	13	4	4	2	34
4	NaOCl (1.1)	—	1.5	51	7	19	7	4	11
5	NaOCl (1.4)	—	4	49	13	21	9	7	0
6	NaOCl (1.4)	$LiClO_4$	0.5	54	0	0	2	7	27
7	NaOCl (1.4)	$NaClO_4$	0.5	48	1	3	1	2	38
8	NaOCl (1.4)	$NaClO_4$	0.5	48[d]	c)	c)	c)	c)	c)
9	NaOCl (1.4)	LiCl	0.5	13	0	10	3	0	74

a) Determined by ^{1}H NMR otherwise noted. b) Determined by UV-vis. c) Not determined. d) Isolated yield.

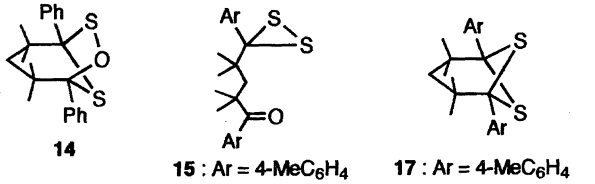
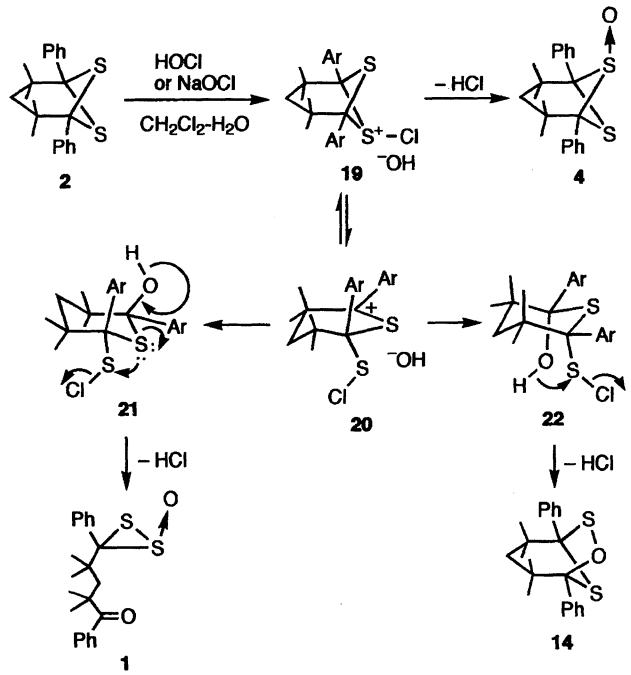


Chart 4.

3*SR*)-dithiirane 1-oxide **1**, dicarbonyl compound **8**, and **4** in the molar ratio of 2 : 1 : 8, indicating that **14** is formed from the starting compound **2** directly. Incidentally, treatment of **14** with HOCl for 8 min gave a mixture of **1**, **8**, and **14** in the molar ratio of 8 : 10 : 9. Thus, the mechanism for the reaction of **2** with HOCl or NaOCl can be speculated as depicted in Scheme 2. Apart from the problem of the true chlorinating species,[23] the reaction must initially give a chlorosulfonium salt **19**[24] which would be in a fast equilibrium with a carbenium ion **20**. Displacement of the chloride ion by a hydroxide ion on the sulfonium sulfur atom of **19** provides the sulfoxide **4**, whereas attack of the hydroxide ion on the carbenium ion center of **20** gives isomeric hydroxy sulfenyl chloride intermediates, **21** and **22**, which eliminate hydrogen chloride to yield **1** and **14**, respectively. The very quick reaction of **2** with HOCl might be ascribed to its fair solubility in organic solvents. Perchlorate ion would shift the equilibrium between **19** and **20** to the latter and enhance the reaction rate. The reason for the dramatic decrease of the yield of **14** caused by addition of perchlorate ion is not clear. Heats of formation of two intermediates, **21** and **22**, calculated by the PM3 method,[25] were 23.6 and 25.0 kcal mol^{-1}, respectively. Their optimized structures are shown in Fig. 4.



Scheme 2.

We have now succeeded in developing two methods for the preparation of dithiiranes from bicyclic 1,3-dithietanes. It is of interest to investigate the applicability of the methods to other types of 1,3-dithietanes. We therefore examined unsymmetric bicyclic 1,3-dithietane **23** and monocyclic 1,3-dithietanes **24**. In the case of the compound **23**, two dithiiranes, **25** and **26**, can be formed (Chart 5). In relation with the mechanism shown in Scheme 2, it is interesting to examine which dithiirane is formed preferably.

The unsymmetrical bicyclic 1,3-dithietane **23** was prepared by reaction of the dicarbonyl compound **27**[26] with Lawesson's reagent (LR) in refluxing benzene in 96% yield along with the bicyclic trithiolane **28** (3%) (Eq. 7). Treatment of a CH_2Cl_2 solution of **23** with aqueous NaOCl–$NaClO_4$ at 0 °C furnished the alkylaryldithiirane **25** in 59% yield (Eq. 8).

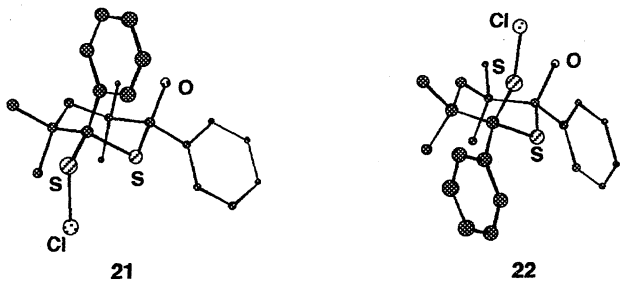


Fig. 4. PM3 optimized structures of **10** and **11** (hydrogen atoms are omitted).

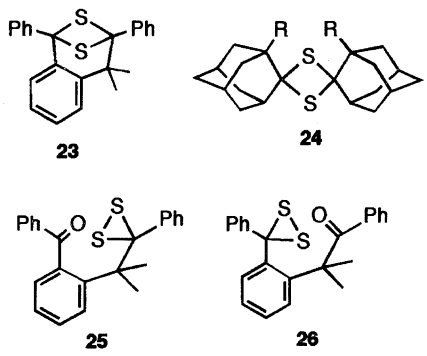
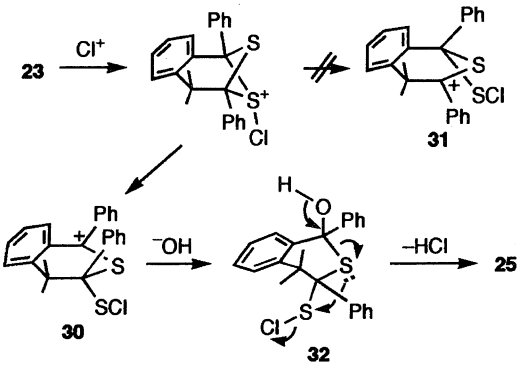
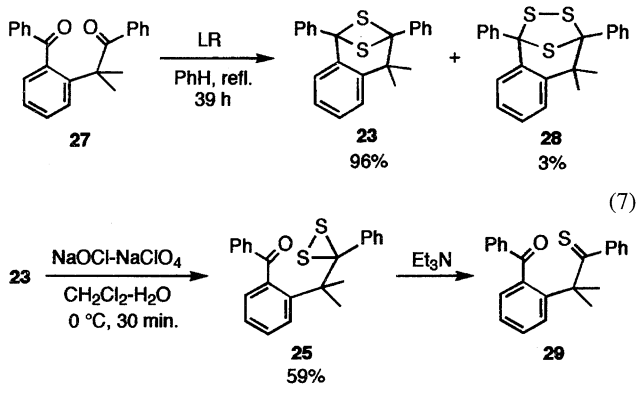


Chart 5.



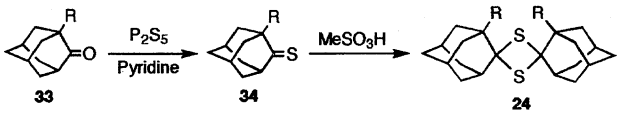
Scheme 3.

Formation of the diaryldithiirane **26** was not detected. The structure of **25** was supported by the spectroscopic data and a chemical transformation. In the ^{13}C NMR spectrum of **25**, the dithiirane carbon resonated at $\delta=76.4$, which is similar to that for the alkylaryldithiirane **3** ($\delta=80.6$), and the carbonyl carbon at $\delta=198.8$. The IR spectrum of **25** showed an absorption at 1661 cm^{-1} assignable to the C=O stretching of a diaryl ketone [cf. 1660 (C=O) cm^{-1} for Ph_2C=O]. In the UV-vis spectrum, λ_{max} appeared at 437 nm (ε 157) [cf. λ_{max} 452 nm (ε 104) for **3**]. In addition, dithiirane **25** decomposed by treating with triethylamine to give the thioketone **29**. The λ_{max} for **29** (556 nm) is very similar to that for an alkyl aryl thioketone **13** (λ_{max} 555 nm) and not to that for Ph_2C=S (λ_{max} 599 nm), supporting the structure of **29**.



The exclusive formation of the dithiirane **25** is explained as shown in Scheme 3. At the initial stage, the carbenium ion intermediate **30**, which is more stable than the other carbenium ion **31** because of conjugation with the aromatic groups and the sulfur atom, is selectively formed. Addition of a hydroxide ion to **30** followed by elimination of HCl from **32** gives the dithiirane **25**. This consideration is in harmony with the mechanism proposed in Scheme 2.

1,3-Dithietanes **24** were prepared by sulfurization of the corresponding 2-adamantanones **33** followed by methanesulfonic acid-catalyzed dimerization of the resulting thioketones **34** (Eq. 9).[27] Oxidation of **24** with MCPBA gave the corresponding oxides **35** (Eq. 10). The geometry of two methyl substituents in **24b** with respect to the 1,3-dithietane ring is cis because the ^1H and ^{13}C NMR spectra of its oxide **35b** shows the two 1-methyladamantyl moieties in **35b** to be equivalent. This relationship holds true for diethyl derivatives **24c** and **35c**. In addition, the structure of **35b** was confirmed by X-ray analysis (Fig. 5, Table 3).



(9)

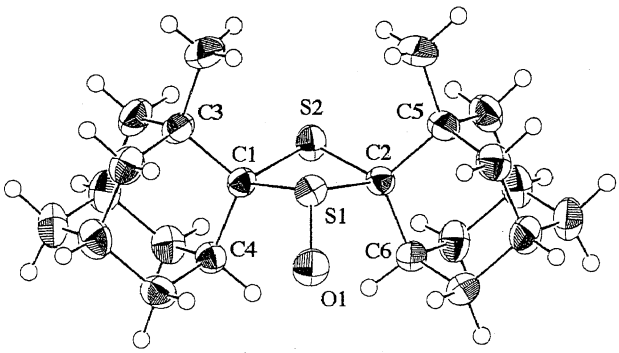
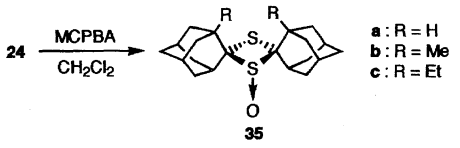


Fig. 5. An ORTEP view of **35b**.

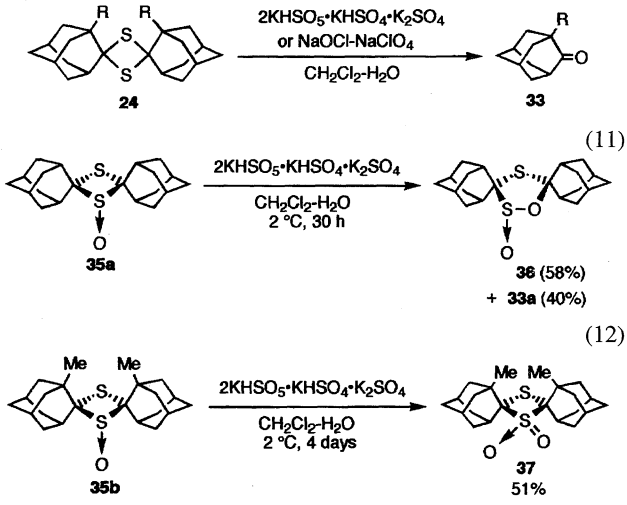
Table 3. Selected Bond Lengths (Å) and Angles (°) Data of **35b**

Bond lengths		Bond angles	
C1–S1	1.866(2)	S1–C1–S2	91.2(1)
C1–S2	1.841(2)	S1–C2–S2	91.4(1)
C1–C3	1.554(3)	C1–S1–C2	85.3(1)
C1–C4	1.539(3)	C1–S2–C2	86.8(1)
C2–S1	1.865(2)	C1–S1–O1	111.5(1)
C2–S2	1.838(2)	C2–S1–O1	111.2(1)
C2–C5	1.552(3)	S1–C1–C3	114.3(2)
C2–C6	1.543(3)	S1–C1–C4	113.5(2)
S1–O1	1.488(2)	S2–C1–C3	113.9(2)
		S2–C1–C4	112.8(2)
		C3–C1–C4	110.2(2)
		S1–C2–C5	114.0(2)
		S1–C2–C6	113.5(2)
		S2–C2–C5	114.1(2)
		S2–C2–C6	112.7(2)
		C5–C2–C6	110.1(2)

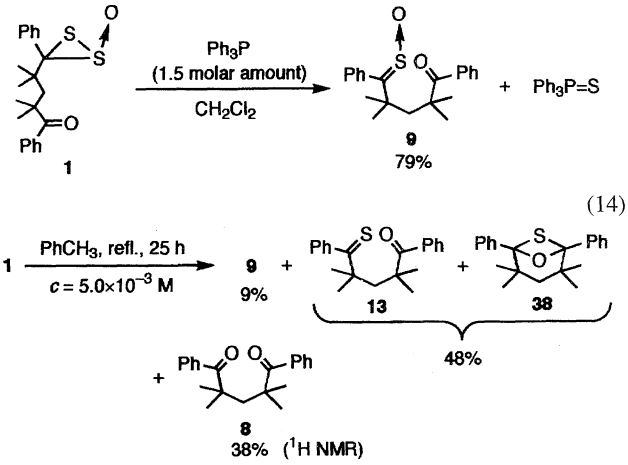


(10)

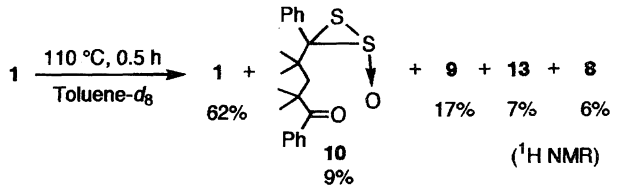
The reaction of **24a** with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (12.5 molar amounts) was carried out without pH control. The reaction under pH-controlled conditions was quite sluggish. Unfortunately, no characteristic coloration due to dithiirane formation was observed throughout the reaction, and workup of the colorless mixture gave only 2-adamantanone **33a** in a high yield (83%). Under similar conditions, **24b** and **24c** were also hydrolyzed to **33b** (60%) and **33c** (90%), respectively. Treatment of dithietanes **24** with NaOCl–$NaClO_4$ also did not give any evidence for the formation of the desired dithiiranes (Eq. 11). Next, attempts to prepare dithiirane oxides from the dithietane oxides **35a** and **35b** were made. The reaction of **35a** with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, however, did not give the desired dithiirane oxide, but gave a 1,2,4-oxadithiolane 2-oxide derivative **36** in 58% yield along with **33a** (40%) (Eq. 12). The reaction of **35b** gave the sulfone **37** in 51% yield (Eq. 13)



Reactivities of Dithiirane Oxides. The divalent sulfur atom of the dithiirane oxide **1** was readily eliminated by treatment with Ph_3P (1.5 molar amount) in CH_2Cl_2 at room temperature to give the thioketone *S*-oxide **9** in 79% yield along with Ph_3P=S (δ_p=44) (Eq. 14). Decomposition of **1** took place on heating to yield the thioketone **13** and the thioketone *S*-oxide **9** with loss of sulfur monooxide and sulfur, respectively, along with the dicarbonyl compound **8** that is formed by further decomposition of **13** and **9** under the applied conditions (Eq. 15). The thioketone **13** exists as an equilibrium mixture with the 6-oxa-7-thiabicyclo[3.1.1]heptane **38**.[13] Thermal stability of **1** in solution depends on concentration. Thus, although 100% decomposition of **1** in a 5.0×10^{-3} M (M=mol dm^{-3}) toluene solution required refluxing of 25 h to give **9** (14%), **13** (48%), and **8** (38%), the decomposition of **1** in a more concentrated solution (2.0×10^{-2} M) was complete within 19 h to give the same compounds in a similar ratio. These observations are indicative of the presence of a decomposition pathway induced by sulfur and/or sulfur monooxide formed. In fact, addition of sulfur (4 molar amounts) accelerated the decomposition of **1** (15 h) in a dilute solution (5.0×10^{-3} M) to give the thioketone *S*-oxide **9**, the dicarbonyl compound **8**, and a trace amount of the thioketone **13**.



Thermal isomerization of **1** to **10** was also observed; heating a solution of **1** in toluene-d_8 (6.4×10^{-2} M) at 110 °C for 0.5 h gave a mixture of **1**, **10**, **9**, **13**, and **8** in the molar ratio of 62 : 9 : 17 : 7 : 6 (Eq. 16). The biradical **39** must be involved as the common intermediate[28] leading to the isomerization and decomposition of **1** (Chart 6).



Reactivities of Dithiiranes. The dithiirane **3** is rather inert to acidic materials such as *p*-toluenesulfonic acid, but very sensitive to nucleophiles such as amines and phosphines. Thus, the dithiirane **3** decomposed quickly by treatment with triethylamine or triphenylphosphine to give the thioketone **13** quantitatively.

It is of great interest to examine whether the dithiirane **3** isomerizes thermally to the corresponding thioketone *S*-sulfide or dithioester.[2,4] A dilute solution of **3** in 1,2-dichloroethane (3.18×10^{-4} M) was heated at reflux at 48 h. An ^{1}H NMR analysis revealed that the bicyclic 1,3,4-oxadi-

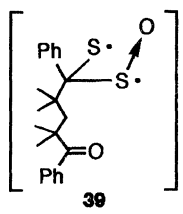
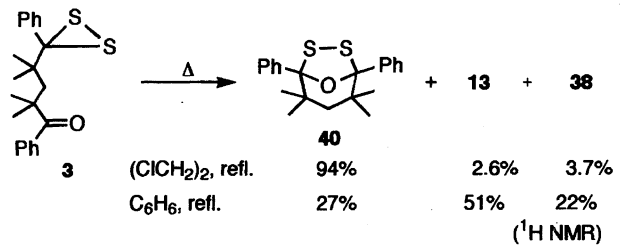


Chart 6.

thiolane **40**[13] was formed in high yield (94%) along with the thioketone **13** (2.6%) and the 1,3-oxathietane **38** (3.7%) (Eq. 17). Interestingly, when heated in refluxing benzene (2.90×10^{-4} M), the yield of **40** markedly decreased to 27% with increased yields of **13** (51%) and **38** (22%). The most straightforward explanation for the formation of **40** involves the isomerization of **3** to the thioketone *S*-sulfide **41** followed by an intramolecular 1,3-dipolar cycloaddition between the thioketone *S*-sulfide and carbonyl moieties (Chart 7). The influence of the solvent polarity would be attributed to the polar character of the thioketone *S*-sulfide functional group. An attempt to trap **41** by intermolecular cycloaddition with dimethyl acetylenedicarboxylate[4] was unsuccessful. Thioketone *S*-sulfides have been considered thermodynamically less stable than the corresponding dithiiranes.[1b] The driving force for the present thermal isomerization of **3** to **41** would be attributed to the rapid intramolecular ring-closure leading to the thermodynamically far more stable compound **40** even if the equilibrium concentration of **41** is very low. No isomerization of **3** to the corresponding dithioester was detected.



(17)

Oxidation of the dithiirane **3** with an equimolar amount of MCPBA in CH_2Cl_2 at 0 °C gave the corresponding dithiirane oxides **1** (87%) and **10** (7%) along with small amounts of the thioketone *S*-oxide **9** and the starting material. On the other hand, oxidation of **3** with dimethyldioxirane (DMD) yielded **1**, **10**, **9**, and **8** in the molar ratio of 81 : 15 : 2 : 1 (Eq. 18). The (1*RS*, 3*SR*)/(1*RS*, 3*RS*) selectivities are 12 for more hindered reagent MCPBA and 5.4 for less hindered DMD. Since isomerization of the (1*RS*, 3*RS*)-dithiirane 1-oxide **10** to the (1*RS*, 3*SR*)-isomer **1** was not brought about by *m*-chlorobenzoic acid, the ratios are kinetically controlled, where the oxidants approach to the dithiirane ring of **3** from the less hindered side to give the (1*RS*, 3*SR*)-oxide **1** as the major product. The further oxidation of **1** with 4 molar amounts of MCPBA yielded the 6,8-dioxa-7-thiabicyclo[3.2.1]octane 7-*exo*-oxide **42** in 23% (Eq. 19). The *exo* stereochemistry of **42** was confirmed by X-ray analysis.[29]

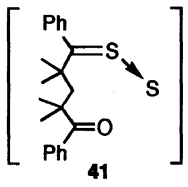
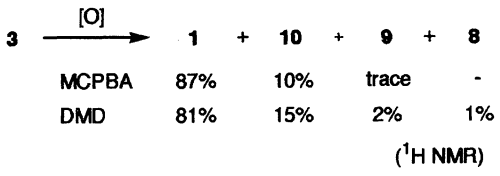
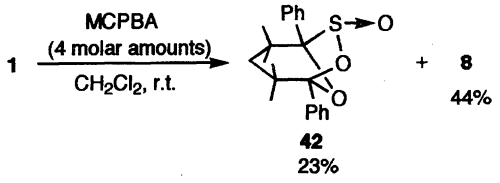


Chart 7.

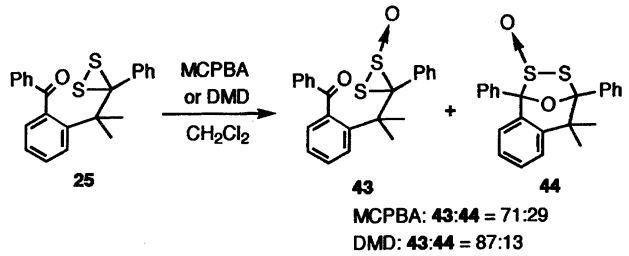


(18)



(19)

Oxidation of the dithiirane **25** with an equimolar amount of MCPBA or DMD gave a 71 : 29 or 87 : 13 mixture, respectively, of the dithiirane oxide **43** and the 1,3,4-oxadithiolane 3-oxide derivative **44** (Eq. 20).



(20)

The dithiirane oxide **43** was not sufficiently stable on silica gel so a part of **43** isomerized to **44** during chromatographic purification (silica gel). Recrystallization of the 87 : 13 mixture did not give the pure dithiirane oxide **43**, either. However, the existence and structure of **43** were supported by the ^{13}C NMR spectrum of the mixture, which showed the signals assignable to the dithiirane carbon (δ=84.0) and the carbonyl carbon (δ=200.1). The compound **44** would be formed by an acid-catalyzed carbonyl insertion to the S(O)–C bond. The structure of **44** was unambiguously confirmed by X-ray structure analysis (Fig. 6, Table 4).

Conclusion

We have succeeded, for the first time, in the preparation of the isolable dithiiranes by oxidative hydrolysis of 6, 7-dithiabicyclo[3.1.1]heptane derivatives. While the dithiiranes are rather stable under neutral or acidic conditions, the readily lose one sulfur atom to give the corresponding thioketonees by treatment with basic materials. On heating, they isomerize to the corresponding 6-oxa-7,8-dithiabicyclo-[3.2.1]octanes through thioketone *S*-sulfides or decompose to the thioketone. Most of the previous attempts to prepare dithiiranes were carried out under basic conditions or at high temperatures. Under such conditions, dithiiranes, even if they formed, would decompose quickly to the corresponding thioketones. Therefore, our successful isolation of dithiiranes largely depends on the neutral to acidic conditions that we have applied. The stability of our dithiiranes should be largely attributed to steric protection by the bulky

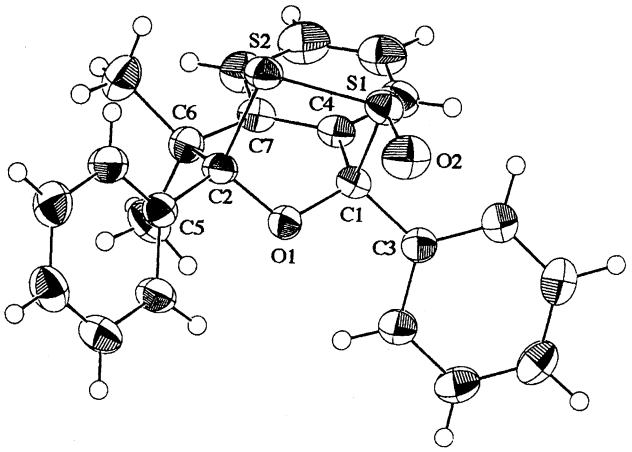


Fig. 6. An ORTEP view of **45**.

Table 4. Selected Bond Lengths (Å) and Angles (°) Data of **45**

Bond lengths		Bond angles	
C1–S1	1.919(2)	S1–C1–O1	103.7(1)
C1–O1	1.398(2)	C1–S1–S2	88.0(1)
C2–S2	1.901(2)	S1–S2–C2	96.7(1)
C2–O1	1.410(2)	S2–C2–O1	105.6(2)
S1–S2	2.085(1)	C1–O1–C2	112.6(2)
S1–O2	1.469(2)	C1–S1–O2	107.4(1)
C1–C3	1.514(3)	S2–S1–O2	110.2(1)
C1–C4	1.515(3)	S1–C1–C3	108.6(2)
C2–C5	1.517(3)	S1–C1–C4	107.3(2)
C2–C6	1.554(3)	O1–C1–C3	108.2(2)
C6–C7	1.525(3)	O1–C1–C4	113.0(2)
C4–C7	1.397(3)	S2–C2–C5	109.6(2)
		S2–C2–C6	109.4(2)
		O1–C2–C5	107.9(2)
		O1–C2–C6	108.7(2)
		C2–C6–C7	108.2(2)
		C4–C7–C6	121.7(2)
		C1–C4–C7	119.2(2)

substituents[30] that prevents the reactive dithiirane ring from intermolecular reactions.[31] The electron-withdrawing character of the phenyl substituent may play an important role as well.

Experimental

General. Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on a Bruker AM400 (400 and 100.6 MHz, respectively) or a Bruker AC200 (200 and 50 MHz, respectively) spectrometers using $CDCl_3$ as the solvent otherwise noted. IR spectra were taken on a Hitachi 270-50 spectrometer. UV-vis spectra were measured using a JASCO V-560 spectrophotometer. Low- and high-resolution mass spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analysis was performed by the Chemical Analysis Center of Saitama University. Throughout this work, the organic layer of the reaction mixture was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Medium-pressure liquid chromatography (MPLC) was performed with an EYELA EFC-2000 using a pre-packed column of Lober® Fertigsäule Größe B (310-25) LiChroprep® Si 60 (40—63 mm) (Merck). $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (OXONE®, Aldrich) was used as purchased. Lawesson's reagent (LR) was prepared from anisol and P_2S_5.[32] Dimethyldioxirane (DMD) was prepared as an acetone solution according to the reported method by oxidation of acetone with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ and its concentration was determined prior to use by oxidizing thioanisole to its sulfoxide with this solution.[33]

Oxidation of 2,2,4,4-Tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane (2) with an Equimolar Amount of MCPBA. To a solution of **2**[6] (687 mg, 2.0 mmol) in CH_2Cl_2 (50 mL) was added purified MCPBA (385 mg, 1.8 mmol) in small portions. After being stirred for 4 h at room temperature, the mixture was quenched with aqueous $NaHSO_3$. The organic layer was separated and washed with aqueous Na_2CO_3 and then water, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give **2** (49 mg, 7%), 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane 6-*endo*-oxide (**4**) (405 mg, 57%), and 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane 6-*exo*-oxide (**5**) (255 mg, 35%) in this order.

4: Colorless needles, mp 232.5—233.5 °C (EtOH). ^{1}H NMR (400 MHz) δ=1.12 (s, 6H), 1.42 (s, 6H), 1.75 (d, J=14.5 Hz, 1H), 3.01 (d, J=14.5 Hz, 1H), 7.26—7.33 (m, 10H); ^{13}C NMR (100.6 MHz) δ=28.8 (q), 29.8 (q), 38.8 (s), 49.3 (t), 87.8 (s), 126.8 (d), 127.8 (d), 128.0 (d), 139.4 (s); IR (KBr) 1082 cm^{-1}. Found: C, 70.65; H, 6.74%. Calcd for $C_{21}H_{24}OS_2$: C, 70.74; H, 6.78%.

5: Colorless needles, mp 229—231 °C (EtOH). ^{1}H NMR (400 MHz) δ=1.20 (s, 6H), 1.28 (s, 6H), 2.08 (d, J=15 Hz, 1H), 2.38 (d, J=15 Hz, 1H), 7.01 (t, J=7 Hz, 4H), 7.25 (d, J=7 Hz, 2H), 7.34 (t, J=7 Hz, 4H); ^{13}C NMR(100.6 MHz) δ=25.6 (CH_3), 27.8 (CH_3), 41.4 (C), 52.6 (CH_2), 77.1 (C), 127.3 (CH), 127.7 (CH), 127.8 (CH), 133.7 (C); IR (KBr) 1092 cm^{-1}. Found: C, 70.56; H, 6.72%. Calcd for $C_{21}H_{24}OS_2$: C, 70.74; H, 6.78%.

Determination of Stereochemistry of 4 and 5. The stereochemistry of sulfoxides **4** and **5** was determined by ^{1}H NMR measurements using Eu(fod)$_3$ as the shift reagent. Shifts of signals of δ=1.12 and 1.42 for **4** and those of δ=1.20 and 1.28 for **5** were as follows [molar ratios of Eu(fod)$_3$ to **4** or **5** were given in parentheses]: **4:** 1.12 (0), 1.36 (0.1), 1.61 (0.2), 1.64 (0.3), 1.82 (0.4), and 2.09 (0.5); 1.42 (0), 1.55 (0.1), 1.70 (0.2), 1.72 (0.3), 1.82 (0.4), and 2.00 (0.5). **5:** 1.20 (0), 1.27 (0.1), 1.35 (0.2), 1.44 (0.3), 1.48 (0.4), and 1.56 (0.5); 1.28 (0), 1.34 (0.1), 1.41 (0.2), 1.49 (0.3), 1.52 (0.4), and 1.60 (0.5). Since larger lower-field shifts were observed for **4** than for **5**, the compound **4** was determined to be *endo* and the other (**5**) *exo*.

Oxidation of 2 with 4 Molar Amounts of MCPBA. To a solution of **2** (341 mg, 1.0 mmol) in CH_2Cl_2 (25 mL) was added dropwise a solution of MCPBA (1.01 g, 4 mmol) in CH_2Cl_2 (30 mL). After being stirred for 21 h at room temperature and then heated at reflux for 44 h, the mixture was cooled to room temperature and quenched with aqueous $NaHSO_3$. The organic layer was separated, washed with aqueous Na_2CO_3 and water, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane *S*,*S*,*S*′-trioxide (**6**) (245 mg, 63%).

6: Colorless crystals, mp 243—250 °C (CCl_4). ^{1}H NMR (400 MHz) δ=1.17 (s, 6H), 1.45 (s, 6H), 1.73 (d, J=15 Hz, 1H), 2.56 (d, J=15 Hz, 1H), 7.36—7.49 (m, 10H); ^{13}C NMR (100.6 MHz) δ=27.6 (CH_3), 30.5 (CH_3), 43.3 (C), 48.4 (CH_2), 112.1 (C), 125.9 (C), 128.5 (CH), 129.0 (CH), 130.3 (CH); IR (KBr) 1316, 1156, 1092 cm^{-1}. MS *m*/*z* 276 ($M^+ - S_2O_3$). Found: C, 64.47: H, 6.02%. Calcd for $C_{21}H_{24}O_3S_2$: C, 70.74; H, 6.78%.

Oxidation of 2 with Hydrogen Peroxide in AcOH. To a

suspension of **2** (341 mg, 1.0 mmol) in AcOH (50 mL) was added hydrogen peroxide (34.5%, 5 mL). The mixture was refluxed for 72 h and cooled to room temperature. The precipitates which separated were collected by filtration to give pure **6** (206 mg, 53%). The filtrate was diluted with water and extracted with CH_2Cl_2. The extracts were washed with water, aqueous Na_2CO_3, and water in this order, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give the dicarbonyl compound **8** (17 mg, 5%) and **6** (97 mg, 25%).

Oxidation of *exo*-Sulfoxide 5 with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (18.4 g, 30 mmol) was dissolved in 150 mL of water and the pH of the solution was adjusted to 5—6 by addition of 1 M KOH. This solution and a few drops of $[Me(C_8H_{17})_3N]^+Cl^-$ were added to a solution of **5** (713 mg, 2 mmol) in CH_2Cl_2 (70 mL). The mixture was stirred at 0 °C for 7 d, adding 1 M KOH (2—3 mL) once or twice a day to maintain the pH of the aqueous layer between 3—6. This resulted in the complete consumption of the starting material **5** (checked by TLC). The organic layer was separated, washed with cold water, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give the dicarbonyl compound **8** (61.6 mg, 10%), a mixture of **8** and (1*RS*, 3*SR*)-3-phenyl-(1,1,3,3-tetramethyl-4-oxo-4-phenylbutyl)dithiirane 1-oxide (**1**) (284.3 mg) (**8**; 11%: **1**; 29%, determined by ^{1}H NMR), pure **1** (208.2 mg, 28%), and a trace amount of 2,2,4,4-tetramethyl-1,5-diphenyl-5-thioxo-1-pentanone *S*-oxide (**9**) in this order.

1: Colorless crystals, mp 124—125 °C (hexane). ^{1}H NMR (400 MHz) δ=0.85 (s, 3H), 1.11 (s, 3H), 1.321 (s, 3H), 1.326 (s, 3H), 2.09 (d, J=14.5 Hz, 1H), 2.26 (d, J=14.5 Hz, 1H), 7.33 (t, J=7.6 Hz, 2H), 7.36—7.46 (m, 6H), 7.55 (d, J=7.6 Hz, 2H); ^{13}C NMR (100.6 MHz) δ=25.4 (CH_3), 27.2 (CH_3), 29.1 (CH_3), 29.2 (CH_3), 42.2 (C), 48.0 (C), 49.9 (CH_2), 87.8 (C), 127.8 (CH), 128.1 (CH×2), 128.8 (CH), 131.1 (CH), 133.0 (C), 133.6 (CH), 138.4 (C), 209.1 (C); IR (KBr) 1673, 1142, 1125 cm^{-1}; MS *m/z* 372 (M^+; trace), 356 (trace), 340 (0.5), 290 (20), 203 (16), 105 (100). Found: C, 67.62; H, 6.51%. Calcd for $C_{21}H_{24}O_2S_2$: C, 67.71; H, 6.49%.

X-Ray Crystal Structure Determination of 1: X-Ray Data for 1: $C_{21}H_{24}O_2S_2$, M_W 372.54. Colorless prisms, 0.40×0.20×0.10 mm, triclinic, space group $P\bar{1}$ (No.2), a=10.289(6), b=10.455(4), c=9.964(6) Å, α=108.28(4), β=109.89(4), γ=88.00(4)°, V=953.9(9) Å^3, D_c=1.297 g cm^{-3}, Z=2, $F(000)$=396, μ(Cu $K\alpha$)=26.10 cm^{-1}. Rigaku AFC5R diffractometer with graphite monochromated Cu $K\alpha$ radiation (λ=1.54178 Å), ω–2θ scan technique to a maximum 2θ value of 120.1°, 3029 reflections measured, 2845 unique reflections. The structure was solved using direct methods (SAPI 91)[34] and refined by a full-matrix least-squares procedure, using 2165 reflections [$I>3\sigma(I)$] for 235 parameters. The non-hydrogen atoms were refined anisotropically. The final R and R_w values are 0.056 and 0.090, respectively.

Tables of the atomic coordinates and B_{eq}, the anisotropic displacement parameters, and all bond lengths, angles, and torsion angles are deposited as Document No. 70007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

9: Colorless oil. ^{1}H NMR (400 MHz) δ=1.32 (s, 6H), 1.41 (s, 6H), 2.27 (s, 2H), 7.17 (d, J=7.2 Hz, 2H), 7.37 (t, J=7.5 Hz, 2H), 7.41—7.50 (m, 4H), 7.60 (d, J=7.2 Hz, 2H); ^{13}C NMR (100.6 MHz) δ=28.0 (CH_3), 28.7 (CH_3), 43.3 (C), 48.4 (C), 48.7 (CH_2), 128.0 (CH), 128.2 (CH), 128.4 (CH), 128.7 (CH), 129.1 (CH), 131.1 (CH), 132.4 (C), 138.6 (C), 208.7 (C), 208.8 (C); IR (KBr) 1674, 1048 cm^{-1}; MS *m/z* 340 (M^+). HRMS. Found: M^+ *m/z* 340.1481. Calcd for $C_{21}H_{23}O_2S$: M, 340.1497.

Oxidation of 5 with an Equimolar Amount of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Reaction of **5** (356 mg, 1.0 mmol) with an equimolar amount of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in the presence of a small amount of $[Me(C_8H_{17})_3N]^+Cl^-$ in CH_2Cl_2 (40 mL) and water (30 mL) at room temperature for 2 d gave 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane *S-endo-S'-exo-S,S'*-dioxide (**7**) (40 mg, 11%) along with **8** (68 mg, 22%), **1** (43 mg, 12%), and **5** (190.5 mg, 53%).

7: Colorless needles, mp 270—271 °C (EtOH). ^{1}H NMR (400 MHz) δ=1.15 (s, 6H), 1.42 (s, 6H), 166 (d, J=14 Hz, 1H), 3.15 (d, J=14 Hz, 1H), 7.38 (t, J=7 Hz, 2H), 7.48 (t, J=7 Hz, 4H), 7.57 (d, J=7 Hz, 4H); ^{13}C NMR (100.6 MHz) δ=26.8 (CH_3), 31.7 (CH_3), 43.3 (C), 48.2 (CH_2), 95.6 (C), 128.50 (CH), 128.53 (CH), 129.2 (CH), 132.7 (C); IR (KBr) 1091, 1083, 1066 cm^{-1}. Found: C, 67.56; H, 6.51%. Calcd for $C_{21}H_{24}O_2S_2$: C, 67.70; H, 6.49%.

Oxidation of *endo*-Sulfoxide 4 with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (12.3 g, 20 mmol) was dissolved in water (80 mL) and the pH of the solution was adjusted to 5—6 by addition of 1 M KOH. This solution and a few drops of $[Me(C_8H_{17})_3N]^+Cl^-$ were added to a solution of **4** (713 mg, 2 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred at 0 °C for 11 d. During the reaction 1 M KOH (2—3 mL) was added once or twice a day to maintain the pH of the aqueous layer between 3—6. The organic layer was separated, washed with cold water, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, $CHCl_3$) to give (1*RS*, 3*SR*)-dithiirane 1-oxide **1** (120 mg, 16%) and a mixture of the starting sulfoxide **4**, dicarbonyl compound **8**, and (1*RS*, 3*RS*)-3-phenyl-3-(1,1,3,3-tetramethyl-4-oxo-4-phenylbutyl)dithiirane 1-oxide (**10**). The fraction containing **10** was subjected to MPLC ($CHCl_3$) repeatedly to give **10** (15 mg, 2%) which is contaminated with a small amount of **1**.

10: Colorless crystals, mp 110—114 °C (Hexane). ^{1}H NMR (400 MHz) δ=1.27 (s, 3H), 1.37 (s, 3H), 1.38 (s, 3H), 1.40 (s, 3H), 2.42 (d, J=14.4 Hz, 1H), 2.64 (d, J=14.4 Hz, 1H), 7.28 (s, 5H), 7.33 (t, J=7.6 Hz, 2H), 7.43 (t, J=7.4 Hz, 1H), 7.62 (d, J=7.3 Hz, 2H); ^{13}C NMR (100.6 MHz) δ=26.4 (CH_3), 28.0 (CH_3), 29.0 (CH_3), 29.6 (CH_3), 44.0 (C), 48.4 (C), 50.0 (CH_2), 84.3 (C), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 131.0 (CH), 131.3 (CH), 136.9 (C), 138.7 (C), 208.5 (C); IR (KBr) 1669, 1118, 1099 cm^{-1}; MS *m/z* 372 (M^+; 0.15), 356 (2.4), 340 (0.7), 324 (0.4), 292 (21), 252 (31), 203 (52), 105 (100). HRMS. Found: M^+, *m/z* 372.1196. Calcd for $C_{21}H_{24}O_2S_2$; M, 372.1218.

X-Ray Crystal Structure Determination of 10. X-Ray data for **10**: $C_{21}H_{24}O_2S_2$, M_W 372.54. Colorless prisms, 0.42×0.28×0.18 mm, triclinic, space group $P\bar{1}$ (No.2), a=9.857(3), b=10.029(2), c=10.704(2) Å, α=90.89(2), β=93.25(2), γ=108.00(4)°, V=949.2(4) Å^3, D_c=1.30 g cm^{-3}, Z=2, $F(000)$=395, μ(Cu $K\alpha$)=25.754 cm^{-1}. Mac Science MXC3K diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ=1.54178 Å), ω–2θ scan method in the range 3°<2θ<130°, 3865 reflections measured, 3240 unique reflections. The structure was solved by direct methods using SIR92[35] in the CRYSTAN GM program system and refined by a full-matrix least-squares method using 2910 reflections [$I\geq3\sigma(I)$] for 333 parameters. The non-hydrogen atoms were refined anisotropically. The final R and R_w are 0.0755 and 0.0801, respectively.

Tables of the fractional atomic coordinates and U_{iso}, the anisotropic thermal parameters, all bond lengths, angles, and torsion angles, and the complete F_o-F_c data are deposited as Document No. 70007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Reaction of 2 with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. A solution of **2** (509 mg, 1.5 mmol) in CH_2Cl_2 (500 mL), an aqueous solution (200

mL) of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (13.7 g, 22.4 mmol), the pH of which was adjusted to 7 by adding 1 M KOH, and a catalytic amount (4 drops) of $[Me(C_8H_{17})_3N]^+Cl^-$ were mixed and stirred vigorously in a refrigerator (at ca. 9 °C) for 4 d. During the reaction, the pH of the aqueous layer was adjusted to 7 twice a day by adding 1 M KOH (2—3 mL). The orange organic layer was separated, dried, and evaporated at 0 °C. The residue was dissolved in CH_2Cl_2 (2—3 mL) and the solution was diluted with hexane. The resulting mixture was allowed to stand in a refrigerator and the first white crystalline crop, which consisted of by-products, was removed by filtration; then the filtrate was cooled again in the refrigerator for 2 d. The orange crystals were collected by filtration and purified by MPLC (CH_2Cl_2) to give an orange solid contaminated with a small amount of the thioketone **13**. The crude material was subjected to recrystallization from CH_2Cl_2–hexane to give pure 3-phenyl-3-(1,1,3,3-tetramethyl-4-oxo-4-phenylbutyl)dithiirane (**3**) (139 mg, 26%). By-products of this oxidation consisted of (1*RS*, 3*SR*)-dithiirane 1-oxide **1**, *endo*-sulfoxide **4**, and the dicarbonyl compound **8**, yields of which were not determined.

3: Orange crystals, mp 68—75 °C decomp (hexane–CH_2Cl_2). ^{1}H NMR (400 MHz) δ=1.11 (s, 6H), 1.33 (s, 6H), 2.25 (s, 2H), 7.21 (t, J=7.9 Hz, 2H), 7.27 (t, J=7.9 Hz, 1H), 7.32—7.36 (m, 4H), 7.43 (t, J=7.9 Hz, 1H), 7.59 (d, J=7.9 Hz, 2H); ^{13}C NMR (100.6 MHz) δ=26.3 (CH_3), 29.2 (CH_3), 42.6 (C), 48.5 (C), 50.1 (CH_2), 80.6 (S–*C*–S), 126.5 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 130.9 (CH), 132.1 (CH), 138.7 (C), 141.2 (C), 208.5 (*C*=O); IR (KBr) 1669 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (ε) 452 nm (104); MS *m/z* 356 (M^+; 3.3), 324 (1.5), 292 (13), 252 (28), 203 (43), 105 (100). Found: C, 70.29; H, 6.78%. Calcd for $C_{21}H_{24}OS_2$: C, 70.74; H, 6.78%.

X-Ray Crystal Structure Determination of 3: X-Ray Data for 3: $C_{21}H_{24}OS_2$, M_W 356.54. Orange prisms, 0.30×0.30×0.10 mm, triclinic, space group $P\bar{1}$ (No.2), a=9.927(5), b=10.593(10), c=9.810(6) Å, α=108.22(5), β=108.29(4), γ=90.64(7)°, V=923(1) Å^3, D_c=1.282 g cm^{-3}, Z=2, $F(000)$=380, μ(Cu $K\alpha$)=28.83 cm^{-1}. Rigaku AFC7R diffractometer with graphite monochromated Cu $K\alpha$ radiation (λ=1.54178 Å), ω–2θ scan technique to a maximum 2θ value of 120.2°, 2924 reflections measured, 2741 unique reflections. The structure was solved using direct methods (SIR88)[36] and refined by a full-matrix least-squares procedure, using 2284 reflections [$I>3\sigma(I)$] for 218 parameters. The non-hydrogen atoms were refined anisotropically. The final R and R_w values are 0.047 and 0.071, respectively.

Tables of the atomic coordinates and B_{eq}, the anisotropic displacement parameters, and all bond lengths, angles, and torsion angles are deposited as Document No. 70007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Reaction of 2 with NaOCl. To a solution of **2** (34.2 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) was added aqueous NaOCl (0.028 M, 5 mL, 0.14 mmol) at 0 °C and the mixture was stirred vigorously at 0 °C for 4 h. The organic layer was separated, dried, and evaporated. The ^{1}H NMR spectrum of the residue indicated the formation of dithiirane **3** (49%), (1*RS*, 3*SR*)-dithiirane 1-oxide **1** (13%), oxadithiolane **14** (21%), *endo*-sulfoxide **4** (9%), and the dicarbonly compound **8** (7%), the yields of which were estimated based on the integral ratio of their methylene proton signals.

Reaction of 2 with NaOCl in the Presence of $NaClO_4$. $NaClO_4$ (13.8 mg, 0.113 mmol) was dissolved in aqueous NaOCl (0.056 M, 2.5 mL, 0.14 mmol). This solution was added to a solution of **2** (34.5 mg, 0.101 mmol) in CH_2Cl_2 (30 mL) at 0 °C and the mixture was stirred vigorously for 30 min at 0 °C. The organic layer was separated, dried, and evaporated. The ^{1}H NMR spectrum of the residue indicated the formation of dithiirane **3** (48%), **1** (1%), **14** (3%), **4** (1%), and **8** (2%) along with the recovery of **2** (38%).

On a separate experiment carried out in the same manner as that described above, the mixture was purified by MPLC (CH_2Cl_2) to give pure **3** (17 mg, 48%).

Preparation of 2,2,4,4-Tetramethyl-1,5-bis(4-methylphenyl)-6,7-dithiabicyclo[3.1.1]heptane (17). Preparation of 2,2,4,4-Tetramethyl-1,5-bis(4-methylphenyl)pentane-1,5-dione (45): Compound **45** was prepared according to the reported method.[12] A solution of 2,2,4,4-tetramethylglutaric acid (2.00 g, 10.6 mmol) in THF (12 mL) and benzene (200 mL) was mixed at 0 °C with a solution of 4-methylphenyllithium, prepared from 4-bromotoluene (7.63 g, 42.4 mmol) and lithium (0.65 g, 89 mmol) in Et_2O (33 mL). After being stirred at 0 °C for 1 h and heated at reflux for 1 d, the mixture was quenched with concd H_2SO_4 (20 mL) and ice and extracted with benzene. The extracts were washed with water, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2–CCl_4 1 : 1) to give **45** (1.17 g, 33%).

45: Colorless needles, mp 112—113 °C (hexane). ^{1}H NMR (200 MHz) δ=1.26 (s, 12H), 2.37 (s, 6H), 2.61 (s, 2H), 7.18 (d, J=8 Hz, 4H), 7.60 (d, J=8 Hz, 4H). Found: C, 82.15; H, 8.43%. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39%.

Preparation of 17: A mixture of **45** (689 mg, 2.0 mmol) and LR (828 mg, 2.0 mmol) in toluene (50 mL) was refluxed under argon for 1 d. After the removal of the solvent, the residue was subjected to column chromatography (SiO_2, CCl_4) to give **17** (748 mg, 99%).

17: Colorless crystals, mp 197—198 °C (EtOH). ^{1}H NMR (200 MHz) δ=1.22 (s, 12H), 2.28 [s, 8H (CH_2 and 2CH_3)], 6.81 (d, J=8 Hz, 4H), 7.04 (d, J=8 Hz, 4H); ^{13}C NMR (50 MHz) δ=21.0, 26.8, 41.9 56.7, 64.7, 125.2, 127.8, 136.4, 138.6; MS *m/z* 368 (M^+; 5), 336 (7), 304 (11), 297 (7), 289 (21), 233 (100), 135 (30). Found: C, 74.90; H, 7.69%. Calcd for $C_{23}H_{28}S_2$: C, 74.95; H, 7.66%.

In a manner similar to that described above, 2,2,4,4-tetramethyl-1,5-bis(4-*t*-butylphenyl)-6,7-dithiabicyclo[3.1.1]heptane (**18**) was prepared by the reaction of 2,2,4,4-tetramethyl-1,5-bis(4-*t*-butylphenyl)pentane-1,5-dione (0.40 g, 0.95 mmol) with LR in 72% yield.

18: Colorless crystals, mp 284—285 °C (EtOH). ^{1}H NMR (400 MHz) δ=1.26 [s, 30H (2*t*-Bu and 4CH_3)], 2.29 (s, 2H), 6.85 (d, J=8 Hz, 4H), 7.24 (d, J=8 Hz, 4H); ^{13}C NMR (100.6 MHz) δ=26.8 (CH_3), 31.3 (CH_3), 34.4 (C), 42.0 (C), 56.1 (CH_2), 64.8 (S–*C*–S), 124.1 (CH), 125.1 (CH), 138.6 (C), 149.5 (C); MS *m/z* 452 (M^+; 4), 420 (5), 388 (19), 373 (21), 275 (100), 57 (38). Found: C, 76.98; H, 9.02%. Calcd for $C_{29}H_{40}S_2$: C, 76.93; H, 8.90%.

Preparation of 3-(4-Methylphenyl)-3-[1,1,3,3-tetramethyl-4-(4-methylphenyl)-4-oxobutyl]dithiirane (15). $NaClO_4$ (17 mg, 0.14 mmol) was dissolved in aqueous NaOCl (0.056 M, 2.5 mL, 0.14 mmol). This solution was added to a solution of **17** (37 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) at 0 °C, and the mixture was stirred vigorously for 30 min at 0 °C. The organic layer was separated, dried, and evaporated. The residue was subjected to MPLC (CH_2Cl_2) to give the dithiirane **15** (14.9 mg, 39%).

15: Orange crystals, mp 86—90 °C decomp (CH_2Cl_2–hexane). ^{1}H NMR (400 MHz) δ=1.08 (s, 6H), 1.33 (s, 6H), 2.26 (s, 2H), 2.34 (s, 3H), 2.38 (s, 3H), 7.01 (d, J=8 Hz, 2H), 7.13 (d, J=8 Hz, 2H), 7.21 (d, J=8 Hz, 2H), 7.55 (d, J=8 Hz, 2H); ^{13}C NMR (100.6 MHz) δ=21.0 (CH_3), 21.4 (CH_3), 26.2 (CH_3), 29.3 (CH_3), 42.7 (C), 48.5 (C), 50.3 (CH_2), 80.5 (S–*C*–S), 127.1 (CH), 128.7 (CH), 128.7 (CH), 132.0 (CH), 135.7 (C), 137.7 (C), 138.3 (C), 141.5 (C), 207.7 (C); IR (KBr) 1670 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (ε) 454 nm

(106); MS *m/z* 384 (M^+; 1), 352 (5), 320 (12), 296 (10), 280 (7), 233 (24), 217 (65), 191 (47), 159 (26), 135 (65), 119 (100). HRMS. Found: M^+, *m/z* 384.1568. Calcd for $C_{23}H_{28}OS_2$: M, 384.1581.

Preparation of 3-(4-*t*-Butylphenyl)-3-[4-(4-*t*-butylphenyl)-1,1,3,3-tetramethyl-4-oxobutyl]dithiirane (16). $NaClO_4$ (17.5 mg, 0.14 mmol) was dissolved in aqueous NaOCl (0.056 M, 2.6 mL, 0.14 mmol). This solution was added to a solution of **18** (43 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) at 0 °C and the mixture was stirred vigorously for 30 min at 0 °C. The organic layer was separated, dried, and evaporated. The residue was subjected to MPLC (CH_2Cl_2) to give the dithiirane **16** (16.7 mg, 37%).

16: Yellow-orange, fine needles, mp 111—115 °C decomp (CH_2Cl_2–hexane). ^{1}H NMR (400 MHz) δ=1.11 (s, 6H), 1.31 (s, 9H), 1.33 (s, 6H), 1.34 (s, 9H), 2.27 (s, 2H), 7.23 (d, *J*=8.5 Hz, 2H), 7.27 (d, *J*=8.5 Hz, 2H), 7.37 (d, *J*=8.5 Hz, 2H), 7.60 (d, *J*=8.5 Hz, 2H); ^{13}C NMR (100.6 MHz) δ=26.4 (CH_3), 29.4 (CH_3), 31.1 (CH_3), 31.3 (CH_3), 34.6 (C), 34.9 (C), 42.7 (C), 48.5 (C), 50.4 (CH_2), 80.6 (S–*C*–S), 123.4 (CH), 123.4 (CH), 124.9 (CH), 128.5 (CH), 131.8 (CH), 135.9 (C), 138.2 (C), 150.9 (C), 154.5 (C), 208.0 (C); IR (KBr) 1682 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (ε) 460 nm (120); MS *m/z* 468 (M^+; 0.5), 436 (5), 404 (13), 380 (10), 364 (4), 275 (28), 259 (78), 233 (28), 204 (18), 177 (64), 161 (100), 145 (21), 57 (68). Found: C, 74.4; H, 8.72%. Calcd for $C_{29}H_{40}OS_2$: C, 74.31; H, 8.60%.

Preparation of 8,8-Dimethyl-1,9-diphenyl-10,11-dithiatricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene (23): A mixture of 2-(2-benzoylphenyl)-2-methyl-1-phenyl-1-propanone (**27**)[26] (103 mg, 0.313 mol) and LR (287 mg, 0.705 mmol) in benzene (25 mL) was heated at reflux for 39 h under argon. Yellow precipitates were removed by filtration and the filtrate was evaporated. The residue was subjected to column chromatography (SiO_2, CCl_4) to give a white solid which was recrystallized from hexane to give **23** (108 mg, 96%). Evaporation followed by recrystallization of the filtrate gave 8,8-dimethyl-1,9-diphenyl-10,11,12-trithiatricyclo[7.2.1.0^{2,7}]-undeca-2,4,6-triene (**28**) (3.6 mg, 3%).

23: Colorless needles, mp 193—195 °C decomp (hexane). ^{1}H NMR (200 MHz) δ=1.66 (s, 6H), 6.44 (dd, *J*=1.1,7.7 Hz, 1H), 6.92 (dt, *J*=0.9, 7.5 Hz, 1H), 7.00—7.04 (m, 2H), 7.14 —7.45 (m, 9H), 7.56 (dd, *J*=0.6, 7.7 Hz, 1H); ^{13}C NMR (50 MHz) δ=25.7 (CH_3), 47.8 (C), 53.0 (S–*C*–S), 62.3 (S–*C*–S), 121.1 (CH), 124.2 (CH), 125.4 (CH), 125.9 (CH), 127.2 (CH), 127.3 (CH), 127.6 (CH), 127.8 (CH), 128.5 (CH), 129.2 (CH), 139.7 (C), 140.8 (C), 146.9 (C), 148.2 (C); MS *m/z* 328 (M^+−S; 2.3), 313 (11), 296 (100), 281 (63). Found: C, 76.53; H, 5.59%. Calcd for $C_{23}H_{20}S_2$: C, 76.62; H, 5.59%.

28: Yellow plates, mp 145—146 °C decomp (EtOH). ^{1}H NMR (200 MHz) δ=1.54 (s, 3H), 1.76 (s, 3H), 6.81 (dd, *J*=1.1, 7.9 Hz, 1H), 6.99 (d, *J*=0.7, 7.5 Hz, 1H), 7.17—7.49 (m, 8H), 7.59—7.64 (m, 2H), 7.79 (br s, 2H); ^{13}C NMR (50 MHz) δ=26.2 (CH_3), 32.2 (CH_3), 50.7 (C), 82.1 (S–*C*–S), 90.6 (S–*C*–S), 125.4 (CH), 126.4 (CH), 127.2 (CH), 127.3 (CH), 127.9 (CH), 128.0 (CH), 128.5 (CH), 128.9 (CH), 129.2 (CH), 130.3 (CH), 137.9 (C), 138.4 (C), 139.2 (C), 143.6 (C); MS *m/z* 392 (M^+; 2.2), 328 (91), 313 (100), 296 (78), 202 (63), 121 (80), 77 (85). Found: C, 70.44; H, 5.10%. Calcd for $C_{23}H_{20}S_3$: C, 70.36: H, 5.13%.

Reaction of 23 with NaOCl–$NaClO_4$: To a solution of **23** (100 mg, 0.277 mmol) in CH_2Cl_2 (100 mL) was added a mixture of $NaClO_4$ (48.9 mg, 0.399 mmol) and aq. NaOCl (0.0436 M, 9.0 mL, 0.392 mmol) at 0 °C. The resulting mixture was stirred vigorously for 30 min. The color of the organic layer turned soon from colorless to yellow. The organic layer was separated and dried, and the solvent was removed. The residue was subjected to MPLC (CH_2Cl_2–hexane) to give 64 mg of 3-[1-(2-benzoylphenyl)-1-methylethyl]-3-phenyldithiirane (**25**) as a yellow foam which was contaminated by a small amount of 2-(2-benzoylphenyl)-2-methyl-1-phenyl-1-propanethione (**29**). The yields of **25** and **29** calculated based on the integral ratio in the ^{1}H NMR spectrum were 60 and 1% yields, respectively. Since attempted recrystallization of the yellow foam from several solvents had been unsuccessful, elemental analysis of **25** was carried out for a material obtained by MPLC purification.

25: Yillow foam, mp 39—42 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ=1.47 (s, 6H), 6.94—7.56 (m, 14H); ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ=29.0 (CH_3), 47.0 (C), 76.4 (S–*C*–S), 125.5 (CH), 126.0 (CH), 127.1 (CH), 127.5 (CH), 128.1 (CH), 128.2 (CH), 129.2 (CH), 130.0 (CH), 131.1 (CH), 132.9 (CH), 137.1 (C), 139.3 (C), 141.5 (C), 142.5 (C) 198.8 (C=O); IR (KBr) 1661 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} (ε) 437 nm (157); MS *m/z* 376 (M^+). Found: C, 72.86; H, 5.68%. Calcd for $C_{23}H_{20}OS_2$: C, 73.37; H, 5.35%.

Reaction of Dithiirane 25 with Triethylamine: To a solution of **25** (41.2 mg, 0.11 mmol) in CH_2Cl_2 was added three drops of triethylamine at 0 °C. The color of the solution gradually turned from yellow to purple. After being stirred for 10 min, the mixture was washed with dil HCl twice and water, dried, and evaporated. The residue was subjected to MPLC (hexane–CH_2Cl_2 2 : 1) to give 2-(2-benzoylphenyl)-2-methyl-1-phenyl-1-propanethione (**29**) (21.5 mg, 57 %).

29: Purple oil. ^{1}H NMR (200 MHz) δ=1.78 (s, 6H), 7.02—7.67 (m, 14H); ^{13}C NMR (50 MHz) δ=33.3 (CH_3), 59.4 (C), 125.6 (CH), 127.2 (CH), 128.27 (CH), 128.31 (CH), 128.6 (CH), 129.4 (CH), 130.0 (CH), 130.3 (CH), 133.1 (CH), 137.5 (C), 137.8 (C), 145.1 (C), 147.3 (C), 198.2 (C=O), 255.7 (C=S); UV-vis (CH_2Cl_2) λ_{max} (ε) 556 nm (60).

Preparation of Dispiro[adamantane-2,2′-[1,3]dithietane-4′,2″-adamantane] (24a): Compound **24a** was prepared by the reported method.[27] Thus, 2-adamantanone (1.01 g, 6.71 mmol) was allowed to react with P_2S_5 (376 mg, 1.69 mmol) in pyridine (10 mL) at 90 °C for 13 h. The reaction mixture was poured into hexane (50 mL). The mixture was washed with water, dil HCl, and then water and dried. After the removal of the solvent, the residue was subjected to column chromatography (SiO_2, hexane–C_6H_6 4 : 1) to give adamantane-2-thione (1.00 g, 90%) as an orange solid. A suspension of the thioketone (2.80 g, 16.8 mmol) in methanesulfonic acid (15 mL) was stirred at room temperature for 1 h, which resulted in the separation of a white solid. The mixture was poured into water and the solid was collected by filtration and recrystallized form 1,4-dioxane to give **24a** (2.39 g, 86%).

24a: Colorless needles. ^{1}H NMR (400 MHz) δ=1.61—1.91 (m, 24H), 2.36 (br s, 4H) [lit, ^{1}H NMR (CCl_4) δ=1.46—2.05 (m, 24H), 2.32 (br s, 4H)]; ^{13}C NMR (100.6 MHz) δ=25.7 (CH), 32.6 (CH_2), 36.3 (CH_2), 44.8 (CH_2), 50.5 (S–*C*–S); MS *m/z* 332 (M^+; 21), 166 (100).

In a manner similar to that described above, dispiro[1-methyladamantane-2,2′-[1,3]dithietane-4′,2″-(1″-methyladamantane)] (**24b**) (580 mg, 69%) was obtained by dimerization of 1-methyladamantane-2-thione (**34b**)[37] (842 mg, 4.67 mmol) in methanesulfonic acid (5 mL). The thioketone **34b** was prepared by sulfurization of 1-methyladamantan-2-one[38] with P_2S_5 in pyridine.

34b: Orange solid. ^{1}H NMR (200 MHz) δ=1.18 (s, 3H), 1.74—2.08 (m, 12H), 3.57 (br s, 1H); ^{13}C NMR (50 MHz) δ=28.7 (CH), 29.2 (CH_3) 35.9 (CH_2), 41.1 (CH_2), 48.4 (CH_2), 54.1 (C), 59.1 (CH), 272.2 (C=S).

24b: Colorless needles (1,4-dioxane), mp 180—181 °C. ^{1}H NMR (200 MHz) δ=1.24—1.29 (m, 10H) [1.29 (s, 6H)], 1.43—

1.79 (m, 16H), 2.04—2.10 (m, 4H), 2.62 (br s, 2H); ^{13}C NMR (50 MHz) δ=27.4 (CH), 29.3 (CH_3) 32.9 (CH_2), 35.8 (CH_2), 38.2 (C), 39.5 (CH_2), 46.9 (CH), 55.7 (S–*C*–S); MS *m/z* 360 (M^+; 16), 180 (100). Found: C, 73.31; H, 9.02%. Calcd for $C_{22}H_{32}S_2$: C, 73.27; H, 8.94%.

In a manner similar to that described above, dispiro[1-ethyladamantane-2,2′-[1,3]dithietane-4′,2″-(1″-ethyladamantane)] (**24c**) (388 mg, 75%) was obtained by dimerization of 1-ethyladamantane-2-thione (**34c**) (520 mg, 1.34 mmol) in methanesulfonic acid (3 mL). The thioketone **34c** was prepared by sulfurization of 1-ethyladamantan-2-one[39] with P_2S_5 in pyridine.

34c: Red oil. ^{1}H NMR (200 MHz) δ=0.87 (t, *J*=7.5 Hz, 3H), 1.59—2.09 (m, 14H), 3.56 (br s, 1H); ^{13}C NMR (50 MHz) δ=7.6, 28.6, 33.5, 36.3, 41.4, 45.2, 56.5, 59.9, 272.4 (C=S).

24c: Colorless needles, mp 233—234 °C (1,4-dioxane). ^{1}H NMR (200 MHz) δ=0.78 (t, *J*=7.6 Hz, 6H), 1.10—1.17 (m, 4H), 1.48—2.15 (m, 24H), 2.70 (br s, 2H); ^{13}C NMR (50 MHz) δ=7.6 (CH_3), 27.1 (CH), 31.5 (CH_2), 33.0 (CH_2), 34.3. (CH_2), 35.8 (CH_2), 40.0 (C), 47.3 (CH), 57.7 (S–*C*–S); MS *m/z* 388 (M^+; 27), 194 (100). HRMS. Found: M^+, *m/z* 388.2279. Calcd for $C_{24}H_{36}S_2$, M, 388.2258.

Preparation of Dispiro[adamantane-2,2′-[1,3]dithietane-4′, 2″-adamantane] 1′-Oxide (35a): To a solution of the 1,3-dithietane **24a** (500 mg, 1.50 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of MCPBA (326 mg, 1.8 mmol) at 0 °C. After being stirred at room temperature for 3 h, the mixture was quenched with aqueous $NaHSO_3$. The organic layer was separated, washed with aqueous $NaHCO_3$ and water, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give the oxide **35a** (415 mg, 79%).

35a: Colorless plates, mp 277—278 °C decomp (hexane). ^{1}H NMR (400 MHz) δ=1.70—1.83 (m, 16H), 1.896—1.903 (m, 2H), 1.97—2.00 (m, 2H), 2.21—2.24 (m, 4H), 2.34—2.37 (m, 2H), 2.57 (br s, 2H); ^{13}C NMR (100.6 MHz) δ=25.8 (CH), 26.9 (CH), 33.0 (CH_2), 33.2 (CH_2), 33.9 (CH_2), 35.3 (CH_2), 35.6 (CH), 36.7 (CH_2), 40.8 (CH), 66.9 (S–*C*–S); IR (KBr) 1084 cm^{-1}; MS *m/z* 348 (M^+; 1.8), 332 (2.4), 300 (1.8), 165 (100). Found: C, 68.94; H, 8.19%. Calcd for $C_{20}H_{28}OS_2$: C, 68.92; H, 8.10%.

In a manner similar to that described above, dispiro[1-methyladamantane-2,2′-[1,3]dithietane-4′,2″-(1″-methyladamantane)] 1′-oxide (**35b**) was prepared in 95% yield (1.09 g) by oxidation of **24b** (1.10 g, 3.05 mmol) with MCPBA (659 mg, 3.82 mmol) in CH_2Cl_2 (40 mL).

35b: Colorless plates, mp 234—234.5 °C decomp (hexane). ^{1}H NMR (200 MHz) δ=1.15—2.16 [m, 28H (2CH_3 at δ=1.19], 2.36—2.46 (m, 2H), 2.65—2.68 (m, 2H); ^{13}C NMR (50 MHz) δ=27.3 (CH), 27.5 (CH_3), 27.6 (CH), 33.2 (CH_2), 35.8 (CH_2), 36.3 (CH_2), 37.6 (CH), 37.8 (C), 41.1 (CH_2), 41.8 (CH_2), 71.4 (S–*C*–S); IR (KBr) 1081 cm^{-1}; MS *m/z* 376 (M^+; 1.3), 360 (1.2), 180 (92), 164 (87), 93 (100). Found: C, 70.07; H, 8.64%. Calcd for $C_{22}H_{32}OS_2$: C, 70.16; H, 8.56%.

X-Ray Crystal Structure Determination of 35b. X-Ray Data for 35b: $C_{22}H_{32}OS_2$, M_W 376.61. Colorless prisms, 0.30×0.32×0.30 mm, orthorhombic, space group $P2_12_12_1$ (No.19), *a*=10.999(2), *b*=26.790(6), *c*=6.534(2) Å, *V*=1925.2(8) Å^3, D_c= 1.30 g cm^{-3}, *Z*=4, *F*(000)=815, μ(Cu *K*α)=24.970 cm^{-1}. Mac Science MXC3K diffractometer with graphite-monochromated Cu *K*α radiation (λ=1.54178 Å), ω–2θ scan method in the range 3° < 2θ<140°, 2214 reflections measured, 2121 unique reflections. The structure was solved by direct methods using SIR92[35] in the CRYSTAN GM program system and refined by a full-matrix least-squares method using 2072 reflections [$I \geq 3\sigma(I)$] for 354 parameters. The non-hydrogen atoms were refined anisotropically. The final *R* and R_w are 0.0284 and 0.0281, respectively.

Tables of the fractional atomic coordinates and U_{iso}, the anisotropic thermal parameters, all bond lengths, angles, and torsion angles, and the complete $F_o - F_c$ data are deposited as Document No. 70007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

In a manner similar to that descried above, dispiro[1-ethyladamantane-2,2′-[1,3]dithietane-4′,2″-(1″-ethyladamantane)] 1′-oxide (**35c**) was prepared in 87% yield (88 mg) by oxidation of **24c** (98 mg, 0.25 mmol) with MCPBA (49 mg, 0.28 mmol) in CH_2Cl_2 (20 mL).

35c: Colorless plates, mp 228—229 °C decomp (hexane). ^{1}H NMR (200 MHz) δ=0.82 (t, *J*=7.5 Hz, 6H), 1.06—1.13 (m, 2H), 1.54—2.00 (m, 22H), 2.13—2.20 (m, 2H), 2.40—2.47 (m, 2H), 2.69 (br s, 2H); ^{13}C NMR (50 MHz) δ=7.3 (CH_3), 26.9 (CH), 27.2 (CH), 30.0 (CH_2), 33.4 (CH_2), 35.7 (CH_2), 36.0 (CH_2), 36.3 (CH_2), 37.8 (CH), 39.8 (C), 72.9 (S–*C*–S); IR (KBr) 1081 cm^{-1}; MS *m/z* 404 (M^+; 1.6), 388 (2.5), 194 (70), 178 (50) 160 (100). Found: C, 71.27; H, 9.08%. Calcd for $C_{24}H_{36}OS_2$: C, 71.23; H, 8.97%.

Reaction of 35a with 2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$. To a solution of **35a** (151 mg, 0.432 mmol) in CH_2Cl_2 (135 mL) was added an aqueous solution (30 mL) of 2$KHSO_5$·$KHSO_4$·K_2SO_4 (3.98 g, 6.48 mmol). The pH of the aqueous layer was adjusted to 7 by adding 1 M KOH and then two drops of $[Me(C_8H_{17})_3N]^+Cl^-$ were added to the mixture. The resulting mixture was stirred vigorously in a refrigerator (ca. 2 °C) for 30 h. During the reaction, the pH of the aqueous layer was adjusted to 7 twice by adding 1 M KOH. The organic layer was separated, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give dispiro[adamantane-2,3′-[1,2,4]oxadithiolane-5′,2″-adamantane] 2′-oxide (**36**) (92 mg, 58%) and adamantanone (**33a**) (52 mg, 40%).

36: Colorless needles, mp 165—166 °C (hexane). ^{1}H NMR (400 MHz) δ=1.61—1.97 (m, 20H), 2.07—2.22 (m, 4H), 2.33—2.42 (m, 4H); ^{13}C NMR (100.6 MHz) δ=25.9 (CH), 26.3 (CH), 26.6 (CH), 26.7 (CH), 33.8 (CH_2), 34.0 (CH), 34.4 (CH_2), 34.6 (CH_2), 35.0 (CH_2), 36.1 (CH), 36.2 (CH_2), 36.7 (CH_2), 37.2 (CH_2), 37.4 (CH_2), 38.1 (CH_2), 38.6 (CH_2), 43.1 (CH), 44.1 (CH), 94.7 (S–*C*–S), 117.8 (S–*C*–S); IR (KBr) 1147 cm^{-1}; MS *m/z* 364 (M^+; 1), 300 (9), 214 (40), 166 (48), 150 (100). Found: C, 65.75; H, 7.75%. Calcd for $C_{20}H_{28}O_2S_2$: C, 65.89; H, 7.74%.

Reaction of 35b with 2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$. To a solution of **35b** (138 mg, 0.366 mmol) in CH_2Cl_2 (100 mL) was added an aqueous solution (40 mL) of 2$KHSO_5$·$KHSO_4$·K_2SO_4 (3.38 g, 5.5 mmol). The pH of the aqueous layer was adjusted to 7 by adding 1 M KOH and then two drops of $[Me(C_8H_{17})_3N]^+Cl^-$ were added to the mixture. The resulting mixture was stirred vigorously in a refrigerator (ca. 2 °C) for 5.5 d. During the reaction, the pH of the aqueous layer was adjusted to 7 by adding 1 M KOH twice a day. The organic layer was separated, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, hexane–CH_2Cl_2 1 : 1) to give dispiro[1-methyladamantane-2,2′-[1,3]dithietane-4′, 2″-(1″-methyladamantane)] 1′,1′-dioxide (**37**) (6 mg, 4%) and 1-methyladamantan-2-one (**33b**) (64 mg, 51%).

37: Colorless crystals, mp 221—222 °C decomp (MeOH). ^{1}H NMR (400 MHz) δ=1.32—1.38 [m, 8H (2CH_3 at δ=1.38)], 1.51—1.67 (m, 6H), 1.71—1.77 (m, 4H), 1.82—1.96 (m, 8H), 2.03—2.07 (m, 2H), 2.33—2.37 (m, 2H) 2.45—2.46 (m, 2H); ^{13}C NMR (100.6 MHz) δ=27.09 (CH_3), 27.13 (CH), 27.2 (CH), 35.1 (CH_2), 36.3 (CH_2), 37.6 (CH_2), 39.0 (C), 41.9 (CH), 43.6 (CH_2), 44.9 (CH_2), 99.3 (S–*C*–S); IR (KBr) 1308, 1147 cm^{-1}; MS *m/z* 328 ($M^+ - SO_2$; 100), 180 (71). Found; C, 67.27; H, 8.30%.

Calcd for $C_{22}H_{32}O_2S_2$: C, 67.30; H, 8.22%.

Reaction of (1*RS*, 3SR)-Dithiirane 1-Oxide 1 with Triphenylphosphine. A mixture of the (1*RS*, 3*SR*)-dithiirane 1-oxide **1** (35 mg, 0.093 mmol) and triphenylphosphine (25 mg, 0.095 mmol) in CH_2Cl_2 (7 mL) was stirred for 1 h at room temperature (at the near end of the reaction, 11 mg (0.042 mmol) of triphenylphosphine was added to complete the reaction). After the removal of the solvent, the residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give the thioketone *S*-oxide **9** (25 mg, 79%).

Thermal Reaction of (1*RS*, 3*SR*)-Dithiirane 1-Oxide 1. In a 5.0×10^{-3} M Solution. A solution of the (1*RS*, 3*SR*)-dithiirane 1-oxide **1** (18.8 mg, 0.05 mmol) in toluene (10 mL) was refluxed under argon. The progress of the reaction was traced by TLC analysis and the spot due to **1** disappeared completely after 25 h. The solvent was removed under reduced pressure. The ^{1}H NMR analysis of the residue indicated the formation of the thioketone **13** (48%), the thioketone *S*-oxide **9** (14%), and the dicarbonyl compound **8** (38%).

In the Presence of S_8. A solution of **1** (18.7 mg, 0.05 mmol) and elemental sulfur (6.6 mg, 0.206 mmol) in toluene (10 mL) was refluxed under argon. It took 15 h for the complete disappearance of **1** (cheked by TLC). The solvent was removed under reduced pressure. The ^{1}H NMR analysis of the residue indicated the formation of the thioketone *S*-oxide **9** (78%) and the dicarbonyl compound **8** (22%).

Thermal Reaction of Dithiirane 3. In 1,2-Dichloroethane (3.18×10^{-4} M). A three necked round-bottomed flask, immersed in concentrated nitric acid for 1 d, rinsed with distilled water repeatedly, and dried, was used for the reaction. In the flask fitted with a nitrogen gas inlet, a reflux condenser to which is attached a $CaCl_2$ tube, and a stopper was placed 1,2-dichloroethane (45 mL). The 1, 2-dichloroethane was refluxed for 1 h with bubbling of nitrogen and cooled. To this 1,2-dichloroethane was added the dithiirane **3** (5.11 mg, 0.0143 mmol) quickly; then the gas inlet and the $CaCl_2$ tube were replaced with a stopper and an argon balloon, respectively. The solution was heated under reflux for 48 h and the solvent was removed. The ^{1}H NMR analysis of the residue revealed the formation of the 1,3,4-oxadithiolane **40**[13] (94%), the thioketone **13** (2.6%), and the 1,3-oxathietane **38** (3.7%).

In Benzene (2.90×10^{-4} M). In a manner similar to described above, the dithiirane **3** (16.53 mg, 0.0464 mmol) was heated in benzene (160 mL) under reflux for 48 h. The ^{1}H NMR analysis revealed the formation of the 1,3,4-oxadithiolane **40** (27%), the thioketone **13** (51%), and the 1,3-oxathietane **38** (22%).

Oxidation of Dithiirane 3 with an Equimolar Amount of MCPBA. To a solution of **3** (36 mg, 0.1 mmol) in CH_2Cl_2 (15 mL) was added a solution of MCPBA (17 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The color of the mixture turned from orange to colorless within 5 min. After the mixture was stirred for 30 min, the solvent was removed to give a pale yellow solid. The ^{1}H NMR spectrum of the solid indicated the formation of the (1*RS*, 3*SR*)-dithiirane 1-oxide **1** (87%), the (1*RS*, 3*RS*)-isomer **10** (7%), and the thioketone *S*-oxide **9** (2%) with recovery of **3** (4%).

Oxidation of Dithiirane 3 with an Equimolar Amount of DMD. To a solution of **3** (10 mg, 0.028 mmol) in CH_2Cl_2 (5 mL) was added dimethyldioxirane (0.061 M acetone solution, 0.5 mL, 0.031 mmol) at 0 °C. After the mixture was stirred for 30 min, the solvent was removed to give a colorless solid. The ^{1}H NMR analysis of the solid indicated the formation of the (1*RS*, 3*SR*)-dithiirane 1-oxide **1** (81%), the (1*RS*, 3*RS*)-isomer **10** (15%), the thioketone *S*-oxide **9** (2%), and the dicarbonyl compound **8** (1%).

Oxidation of (1*RS*, 3*SR*)-Dithiirane 1-Oxide 1 with 4 Molar Amounts of MCPBA. To a solution of **1** (126 mg, 0.338 mmol) in CH_2Cl_2 (15 mL) was added a solution of MCPBA (234 mg, 1.35 mmol) in CH_2Cl_2 (10 mL) dropwise over a period of 15 min at 0 °C. After being stirred for 5 h at room temperature, the mixture was washed with aqueous $NaHCO_3$ and water, dried, and evaporated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give 83 mg of a mixture of 2,2,4,4-tetramethyl-1, 5-diphenyl-6,8-dioxa-7-thiabicyclo[3.2.1]octane 7-*exo*-oxide (**42**) and the dicarbonyl compound **8**. The mixture was recrystallized twice from a mixed solvent of CH_2Cl_2 and hexane to give pure **42** (28 mg, 23%) as colorless needles. The other product **8** (46 mg, 44%) was obtained from the filtrates.

42: Colorless needles, mp 216—218 °C (CH_2Cl_2–hexane). ^{1}H NMR (400 MHz) δ=0.97 (s, 3H), 1.05 (s, 3H), 1.12 (s, 3H), 1.29 (s, 3H), 1.41 (d, J=14.6 Hz, 1H), 1.77 (d, J=14.6 Hz, 1H), 7.31—7.39 (m, 8H), 7.67 (dd, J=7.8 and 1.8 Hz, 2H); ^{13}C NMR (100.6 MHz) δ=24.8 (CH_3), 26.7 (CH_3), 27.5 (CH_3), 28.0 (CH_3), 36.7 (C), 39.0 (C), 47.4 (CH_2), 117.2 (C), 125.3 (C), 126.9 (CH×2), 127.4 (CH×2), 128.3 (CH), 128.6 (CH), 133.5 (C), 136.3 (C); IR (KBr) 1147, 1071 cm^{-1}. Found: C, 70.69; H, 6.74%. Calcd for $C_{21}H_{24}O_3S$: C, 70.76; H, 6.79%.

Oxidation of Dithiirane 25 with MCPBA. To a solution of **25** (61 mg, 0.163 mmol) in CH_2Cl_2 (10 mL) was added a solution of MCPBA (36 mg, 0.206 mmol) in CH_2Cl_2 (10 mL) dropwise at 0 °C. After being stirred for 20 min at 0 °C, the mixture was quenched with aqueous $NaHSO_3$. The organic layer was separated, washed with aqueous $NaHCO_3$ and then water, dried, and evaporated. The ^{1}H NMR spectrum showed that the residue was a 71 : 29 mixture of the dithiirane oxide **43** and 8,8-dimethyl-1,9-diphenyl-12-oxa-10, 11-dithiatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene 11-oxide (**44**). The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give 52 mg of a mixture of **43**, **44**, and the dicarbonyl compound **27**; the molar ratio of **43** : **44** was 25 : 75 by ^{1}H NMR analysis. Recrystallization of the mixture from a mixed solvent of hexane and CH_2Cl_2 gave pure **44** (12.5 mg, 20%).

44: Colorless plates, mp 182—185 °C decomp (EtOH). ^{1}H NMR (200 MHz) δ=1.39 (s, 3H), 1.55 (s, 3H), 7.08—7.59 (m, 10H), 7.68—7.72 (m, 2H), 7.89—7.94 (m, 2H); ^{13}C NMR (50 MHz) δ=22.0 (CH_3), 30.3 (CH_3), 45.4 (C), 110.9 (S–*C*–S), 118.5 (S–*C*–S), 125.8 (CH), 125.96 (CH), 126.01 (CH), 127.5 (CH), 128.1 (CH), 128.4 (CH), 128.8 (CH), 129.2 (CH), 129.30 (CH), 129.35 (C), 130.1 (CH), 135.0 (C), 138.6 (C), 141.7 (C); IR (KBr) 1107 cm^{-1}; MS *m/z* 328 (M^+−O−SO; 6), 313 (6), 223 (100). Found: C, 70.28; H, 5.11%. Calcd for $C_{23}H_{20}O_2S_2$: C, 70.38; H, 5.14%.

X-Ray Crystal Structure Determination of 44. X-Ray data for **44**: $C_{23}H_{20}O_2S_2$, M_W 392.50. Colorless prisms, 0.40×0.46×0.30 mm, monoclinic, space group $P2_1/n$ (No.14), a=15.850(3), b=8.561(2), c=14.059(3) Å, β=91.94(2), V=1096.6(7) Å^3, D_c=1.37 g cm^{-3}, Z=4, $F(000)$=823, μ(Cu $K\alpha$)=25.990 cm^{-1}. Mac Science MXC3K diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ=1.54178 Å), ω–2θ scan method in the range 3° < 2θ<130°, 4135 reflections measured, 3392 unique reflections. The structure was solved by direct methods using SIR92[35] in the CRYSTAN GM program system and refined by a full-matrix least-squares method using 3166 reflections [$I\geq3\sigma(I)$] for 319 parameters. The non-hydrogen atoms were refined anisotropically. The final R and R_w are 0.0393 and 0.0401, respectively.

Tables of the fractional atomic coordinates and U_{iso}, the anisotropic thermal parameters, all bond lengths, angles, and torsion angles, and the complete F_o-F_c data are deposited as Document No. 70007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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References

1) a) J. P. Snyder and L. Carlsen, *J. Am. Chem. Soc.*, **99**, 2931 (1977); b) S. P. So, *J. Mol. Struct. (Theochem.)*, **148**, 153 (1986); c) R. M. Wilson, D. N. Buchanan, and J. E. Davis, *Tetrahedron Lett.*, **1971**, 3919, and references cited therein.

2) a) A. Senning, H. C. Hansen, M. F. Abdel-Megeed, W. Mazurkiewicz, and B. Jensen, *Tetrahedron*, **42**, 739 (1986); b) A. Senning, *Sulfur Lett.*, **4**, 213 (1986); c) A. Senning, *Sulfur Lett.*, **11**, 83 (1990); d) G. W. Kutney and K. Turnbull, *Chem. Rev.*, **82**, 333 (1982); e) A. Senning, *Main Group Chem. News*, **2**, 33 (1994).

3) A. Ishii, T. Akazawa, M.-X. Ding, T. Honjo, J. Nakayuama, M. Hoshino, and M. Shiro, *J. Am. Chem. Soc.*, **115**, 4914 (1993).

4) R. Huisgen and J. Rapp, *J. Am. Chem. Soc.*, **109**, 902 (1987).

5) a) R. W. Murray, *Chem. Rev.*, **89**, 1187 (1989); b) W. Adam, R. Curci, and J. O. Edwards, *Acc. Chem. Res.*, **22**, 205 (1989); c) J. O. Edwards, R. H. Pater, R. Curci, and F. DiFuria, *Photochem. Photobiol.*, **30**, 63 (1979).

6) A. Ishii, J. Nakayama, M.-X. Ding, N. Kotaka, and M. Hoshino, *J. Org. Chem.*, **55**, 2421 (1990).

7) A. Ishii, M.-X. Ding, K. Maeda, J. Nakayama, and M. Hoshino, *Bull. Chem. Soc. Jpn.*, **65**, 3343 (1992).

8) A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshino, and M. Shiro, *Angew. Chem., Int. Ed. Engl.*, **33**, 777 (1994).

9) A. Ishii, T. Maruta, K. Teramoto, and J. Nakayama, *Sulfur Lett.*, **18**, 237 (1995).

10) A. Ishii, Y.-N. Jin, H. Nagaya, M. Hoshino, and J. Nakayama, *Tetrahedron Lett.*, **36**, 1867 (1995).

11) For oxidation of sulfides with OXONE®, see: a) R. J. Kennedy and A. M. Stock, *J. Org. Chem.*, **25**, 1901 (1960); b) B. M. Trost and D. P. Curran, *Tetrahedron Lett.*, **22**, 1287 (1981).

12) G. Maier, C. Roth, and R. K. Schmitt, *Chem. Ber.*, **118**, 704 (1985).

13) A. Ishii, M.-X. Ding, J. Nakayama, and M. Hoshino, *J. Chem. Soc., Chem. Commun.*, **1992**, 7; A. Ishii, M.-X. Ding, J. Nakayama, and M. Hoshino, *Bull. Chem. Soc. Jpn.*, **66**, 1714 (1993).

14) F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.

15) K. Okiya, C. Hirose, D. G. Lister, and J. Sheridan, *Chem. Phys. Lett.*, **24**, 111 (1974).

16) a) J.-G. Gourcy, G. Jeminet, and J. Simonet, *J. Chem. Soc., Chem. Commun.*, **1974**, 634; b) Q. N. Porter and J. H. P. Utley, *J. Chem. Soc., Chem. Commun.*, **1978**, 255; c) D. Ghiringhelli, *Synthesis*, **1982**, 580; d) L. Mathew and S. Sankararaman, *J. Org. Chem.*, **58**, 7576 (1993); e) K. Tanemura, H. Dohya, M. Imamura, T. Suzuki, and T. Horaguchi, *Chem. Lett.*, **1994**, 965.

17) J. Cossy, *Synthesis*, **1987**, 1113.

18) G. A. Olah, S. C. Narang, and G. F. Salem, *Synthesis*, **1980**, 657.

19) Aqueous HOCl was prepared in situ by treatment of a solution of $Ca(OCl)_2$ with solid CO_2: S. G. Hegde, M. K. Vogel, J. Saddler, T. Hrinyo, N. Rockwell, R. Haynes, M. Oliver, and J. Wolinsky, *Tetrahedron Lett.*, **21**, 441 (1980).

20) A. Ishii, Y.-N. Jin, M. Hoshino, and J. Nakayama, *Heteroatom Chem.*, **6**, 161 (1995).

21) Sodium hypochlorite solution (Kanto Chemical Co., Inc.) was used after dilution of 15 or 30 times.

22) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958); J. D. Simon and K. S. Peters, *J. Am. Chem. Soc.*, **104**, 6142 (1982), and references cited therein.

23) C. G. Swain and D. R. Crist, *J. Am. Chem. Soc.*, **94**, 3195 (1972).

24) L. S. S. Réamonn and W. I. O'Sullivan, *J. Chem. Soc., Chem. Commun.*, **1976**, 1012; L. S. S. Réamonn and W. I. O'Sullivan, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 1194; M. T. M. El-Wassimy, K. A. Jørgensen, and S.-O. Lawesson, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 2201.

25) MOPAC Ver. 6, J. J. P. Stewart, *QCPE Bull.*, **9**, 10 (1989).

26) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

27) J. W. Greidanus, *Can. J. Chem.*, **48**, 3530 (1970).

28) R. W. Hoffmann and W. Barth, *J. Chem. Soc., Perkin Trans. 2*, **1983**, 1687.

29) The mechanism of the formation of **42** and its X-ray structure analysis will be reported elsewhere.

30) A. Ishii, M.-X. Ding, J. Nakayama, and M. Hoshino, *Chem. Lett.*, **1992**, 2289.

31) W. Chew and D. N. Harpp, *Tetrahedron Lett.*, **33**, 45 (1992).

32) B. S. Pedersen, S, Scheibye, N. H. Nilsson, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 223 (1978).

33) W. Adam, L. Hadjiarapoglou, and A. Smerz, *Chem. Ber.*, **124**, 227 (1991).

34) Fan Hai-Fu, "Structure Analysis Programs with Intelligent Control," Rigaku Corporation, Tokyo, Japan (1991).

35) A. Altomare, G. Cascarano, C. Giacovazzo, and A. Guagliardi, *J. Appl. Crystallogr.*, **26**, 343 (1993).

36) M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, and D. Viterbo, *J. Appl. Crystallogr.*, **22**, 389 (1989).

37) F. Cordt, R. M. Frank, and D. Lenoir, *Tetrahedron Lett.*, **1979**, 505.

38) W. H. W. Lunn, *J. Chem. Soc. C*, **1970**, 2124; D. Lenoir, R. Glaser, P. Mison, and P. R. Schleyer, *J. Org. Chem.*, **36**, 1821 (1971).

39) D. Lenoir, R. M. Frank, F. Cordt. A. Gieren, and V. Lamm, *Chem. Ber.*, **113**, 739 (1980).