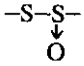
SMALL RING COMPOUNDS CONTAINING SULFUR ATOMS

Shigeru Oae

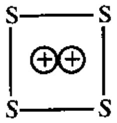
Institute of Heteroatom Chemistry, 2509 Hirao, Mihara-cho, Minamikawachi-gun, Osaka, 587 Japan

Abstract - Small ring compounds containing sulfur atoms, especially three and four membered heterocycles, were reviewed in the light of recent findings and hypotheses.

INTRODUCTION

Ring compounds can be made from three membered cycle. The smallest ring containing all sulfur atoms is the cyclic S_3 species. If all three atoms can utilize each one lone pair, it would form six π–electrons and be capable of forming an aromatic ring, since the ring would have to be in the same plane. However, no such a ring has been observed yet. Three membered ring compounds containing two sulfur atoms have been made and their chemistries are briefly mentioned. Recently, three membered ring containing thiolsulfinate,  $-S-\underset{\overset{\downarrow}{O}}{S}-$, in the molecule has been made, while that containing disulfide group, −S−S−, has also been prepared. Their chemistries are also mentioned. The chemistry of two carbon atoms-containing three membered rings is quite well known. Episulfones have been isolated sucessfully and are known to be the key intermediate in the Ramberg-Bäcklund reaction, however, they are not as stable as the thiirene 1,1-dioxide, since the latter is aromatic, and obeys 4n + 2 rule, in which n = 0.

Ring compounds containing all four sulfur atoms were not isolated as a neutral species, but as doublly positively-charged species (**1**). However, no neutral species has ever been isolated yet.

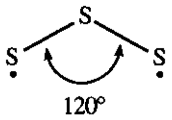


1

What about a heterocyclic ring which has one carbon atom and three sulfur atoms ? No neutral species nor any charged species has ever been prepared successfully. There is no reason why these species have not been made. Numerous examples have been known for heterocycles which have two carbon atoms and two sulfur atoms and their chemistries have pretty well settled, while thietanes and their derivatives, which have three carbon atoms and only one sulfur atom, are well known and quite a number of well-documented reviews are available,[1] and hence they are not included. All these three-membered sulfur containing heterocycles and a part of four-membered rings are reviewed in the light of mechanistic thinkings and also the past information.

THREE-MEMBERED RINGS

The S_3 allotrope of the ground state is believed to be a biradical species and has the following structure (**2**),[2] and it is known to be prepared in benzene solution by the following reaction (Scheme 1) and to have a deep red color.



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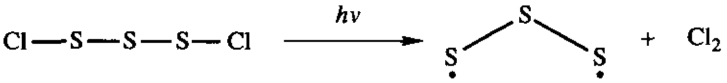
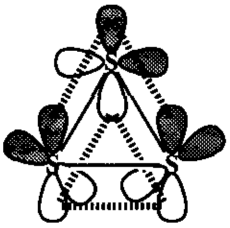


Scheme 1

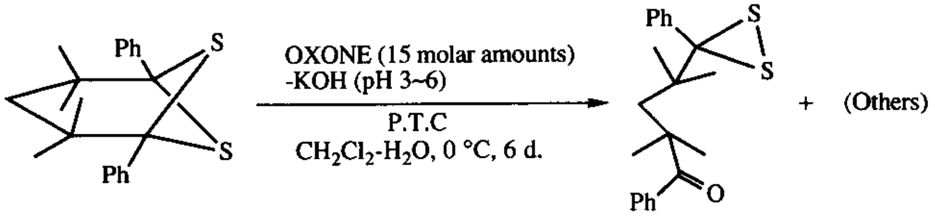
This S_3 allotrope is believed to be responsible for many reactions involving elemental sulfur at high temperature.[3] However, if all three sulfur atoms could be equivalent and lie in the same ring, the ring would be able to assume six π-electron system and hence could be aromatic, since it could obey 4n + 2 Hückel's rule of aromaticity. Why this molecule (**3**) has not been the target of research work ?



3

Although this species (**3**) could be made or trapped, nobody has shown any interest. Or it could be so difficult to observe. Perhaps, one can still make a theoretical calculation of this molecule.

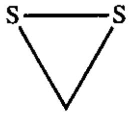
The first isolation of a dithiirane derivative, whose skeletal framework is shown in Scheme 2, has recently be made.[4]



Scheme 2

4 (20 %)

Although the parent molecule (**5**) has not been made yet, heavy substituents attached to dithiirane may be responsible for the successful isolation of the molecule (**4**), which was made in the reaction shown in Scheme 2, while the molecule has the following characteristic properties, while X-ray crystallographic study also confirms the presence of the dithiirane orange crystals (**4**).



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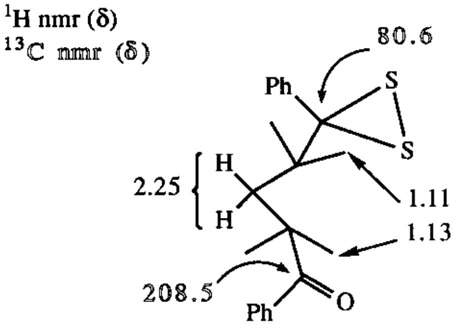


4

Orange crystals

mp 68-75 °C (decomp.)

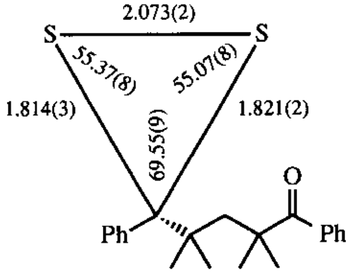
ir (KBr) 1669 cm^{-1} (C=O)

uv-vis (CH_2Cl_2) λ_{max} 451 nm (ε 107)

(cf.  λ_{max} 422 nm by CNDO/S-Cl)

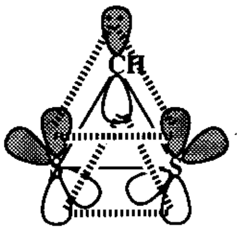
ms *m/z* 356 (M^+, 3.3%), 105 (100)

Bond distances (Å) and bond angles (deg)



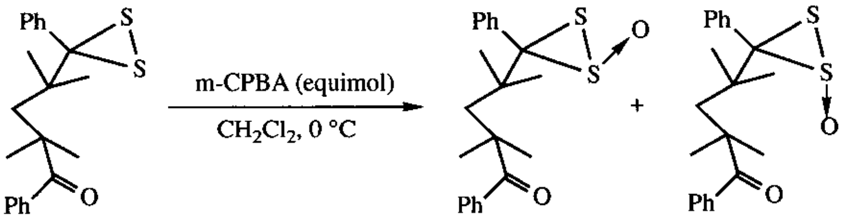
(cf. S_8: γ_{S-S} 2.06 Å;  : γ_{C-S} 1.819 Å; Me_2S: γ_{C-S} 1.82 Å)

The carboanion of the dithiirane ring (**6**) could also obey Hückel's rule of aromaticity, however, it has never been made. Perhaps, for the same reason, the molecule has not been looked at.



6

The dithiirane monoxide has been synthesized in the following way (Scheme 3).[5]

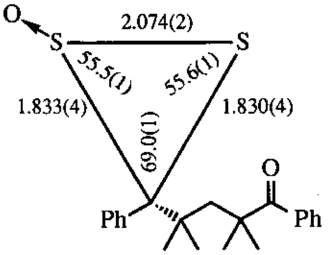


5 **7** (87%) **8** (7%)

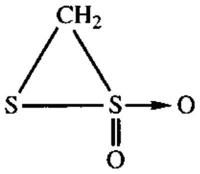
Scheme 3

According to the X-ray crystallographic analysis of **7**, none of the bonds is unusual as shown below.

Bond distances (Å) and bond angles (deg)



The next step would be the synthesis of the following dithiirane dioxide (**9**). Probably, by applying the nucleophilic oxidant,[6] it can be successfully made.



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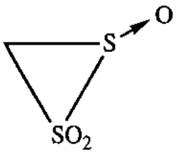
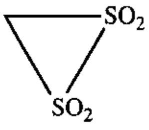
In connection with these, none of dithiirane trioxide (**10**), nor tetraoxide derivatives (**11**) have been prepared yet.



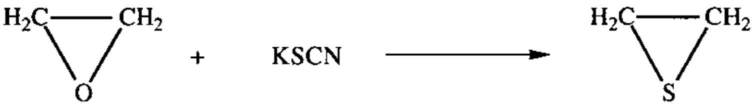
10



11

The former trioxide (**10**) would be rather difficult to be made because of the unstable of the compounds,[7] the latter tetraoxide (**11**) would be successfully prepared. However, no attempt has been made.

Thiirane has been looked at by many investigators. One of the standard procedures is shown in Scheme 4.[8]

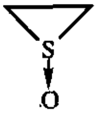
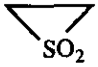


Scheme 4

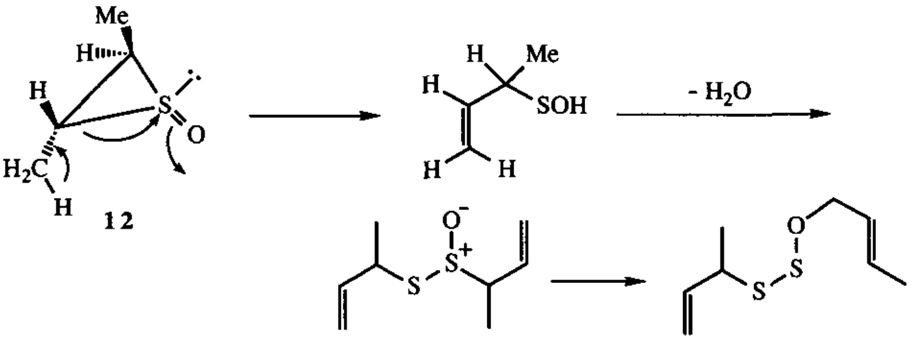
Though there are many other ways to prepare it and its derivatives,[9] this review is not elaborating the procedures. However, from early period on, there are a few theoretical treatments.[10] It would be interesting to compare the bond distances and angles of thiirane and the monooxide and the dioxide (Table 1).

It is interesting to compare the bond distances of both C—C and C—S. As oxidation proceeds, C—C bond distance become longer, while C—S bond distance become shorter, probably because of the increase of the steric bulkiness. Meanwhile, the bond angle of ∠C—S—C is getting wider again, because of the increase of the steric bulkiness. Even without running the actual experiment, one can presume many interesting chemical behaviors.

Table 1. Bond Distances and Bond Angles

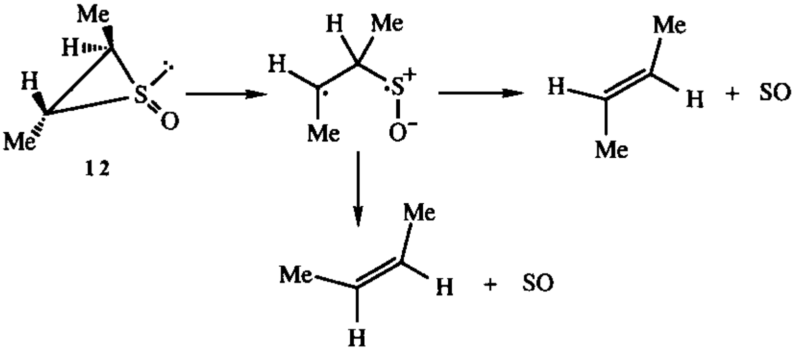
	Bond Distance (Å) C—C	Bond Distance (Å) C—S	Angle (deg) C–S–C	Ref.
	1.49	1.819	48.5	11
	1.515	1.788	50.1	12
	1.560	1.757	52.7	12

Apart from many interesting reactions of thiirane and its derivatives which are not dealt here, a few interesting reactions of thiirane sulfoxide are shown here. One is the work of Kondo *et al.*,[13] while the others are somewhat similar ones.[14,15] Thiirane 1-oxides bearing alkyl groups *cis* to sulfonyl oxygen are unstable. For example, *trans*-2,3-dimethylthiirane 1-oxide (**12**) decomposes readily to a sulfonic acid, due probably to release the inherent strain of the ring. Baldwin *et al.*, were able to trap the sulfenic acid, which was converted to 2-mercaptobut-3-enes (Scheme 5).[15]



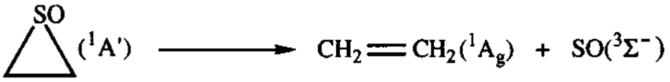
Scheme 5

In the rapid thermolysis of the thiirane (**12**), [2,3] sigmatropic rearrangement takes place around 200-340 °C to afford the final sulfenate (**13**). At a much higher temperature, apparently biradical intermediate would give the final products, favoring a high stereospecificity (*cis* : *trans* = 95 : 5 at 200 °C) (Scheme 6).



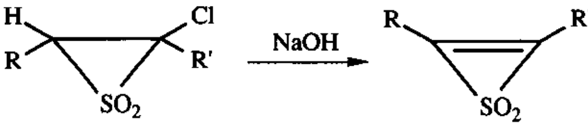
Scheme 6

Pyrolysis of thiirane monoooxide was monitored,[16] and a little later a more carefull study has shown to involve the formation of triplet SO, as shown in Scheme 7.[17]



Scheme 7

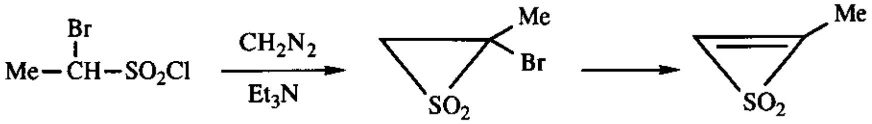
The synthesis and thermal decomposition of thiirane-1,1-dioxides and their derivatives are very much studied, in connection to the famous Ramberg-Bäcklund reaction[18] and is not reviewed here, however, thiirene dioxide and its derivatives are quite stable and can be nicely isolated (Scheme 8).[19,20] It obeys the Hückel's rule of aromaticity, 4n + 2 with n = 0 and is known to be much more than thiirane dioxide.



R = Me, Ph, $PhCH_2$, PhCHMe
R'= Me, Ph, H

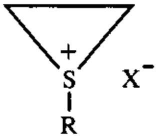
Scheme 8

Carpino *et al.*, first synthesized a thiirane dioxide in the following manner (Scheme 9).[20]



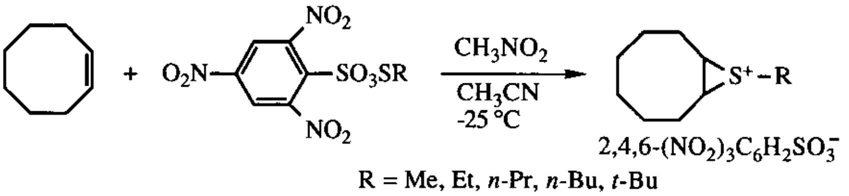
Scheme 9

Thiiranium (episulfonium ions) (**13**) is very well known,[1] since it is known to be involved as the intermediate of either in the solvolysis of β-haloethyl sulfide and similar compounds and in the addition of the sulfenyl halides to olefins. Even alkylation of the thiirane can achieve to obtain it.



13

However, the studies are so numerous that much of the formations of the thiiranium ions are not mentioned here. One of stable thiiranium ions isolated was the following reaction by Pettit and Helmkamp (Scheme 10).[21]

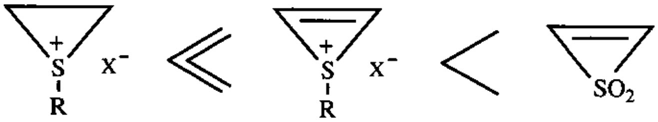


Scheme 10

Indeed, the thiiranium hexachloroantimonate is said to be stable for a few weeks at -20 °C when moisture is excluded. However, it is not as stable as the thiirenium ions, some of which has a clear melting point above 100 °C.

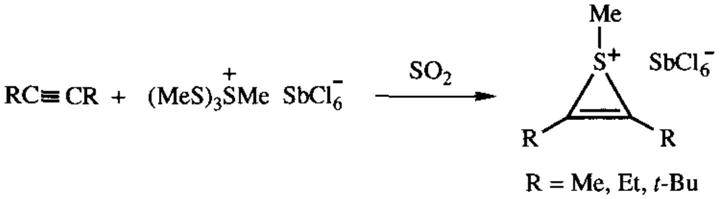
Although the sulfonio group is slightly more electron-withdrawing than the sulfonyl group in view of the acid-enhancing effect,[22,23] the instability of the thiirenium ions to that of the thiirane dioxide may be due partly to the availability of the lone electron pair, thus the Hückel's rule of aromaticity, 4n + 2 does not hold well. Instead, a small portion of some *anti* -aromaticity may be functioning, though thiirenium ions, shown below, are much more stable than the corresponding thiiranium ions, as described before.

Aromaticities



Meanwhile, thiirene dioxide is known to hold the aromaticity rule, because of the non-availability of the lone electron pair on the sulfur atom.

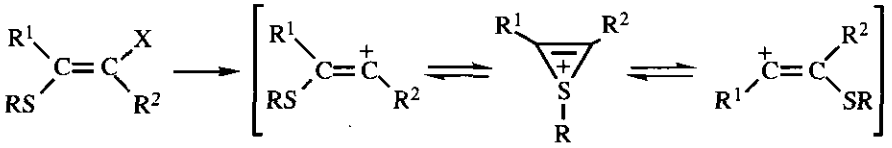
The standard procedure of preparing thiirenium salt is the addition of sulfenyl derivatives to acetylenes as shown in Scheme 11.[1,24]



Scheme 11

Though trimethyl thiirenium salt is unstable above -40 °C, di-*t*-butyl derivative can be precipitated from pentane as white crystals of mp 151-152 °C and is known to be stable at room temperature.[1,25]

Although thiirenium ions have not been isolated, chemical and stereochemical data as well as kinetic data appear to support the intervention of the thiirenium ions in the following solvolytic reaction (Scheme 12).[1,26]

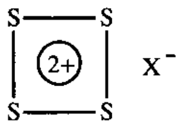


Scheme 12

FOUR-MEMBERED RINGS

There are many interesting compounds among four-membered heterocycles containing sulfur atoms, however, discussions were limited only on the four-sulfur atoms ring compound and that with three sulfur atoms and one carbon atom.

The four-membered ring containing four sulfur atoms can be formed as the dications (**14**), shown below,[27] and was first detected in solution of sulfur in 30% fuming sulfuric acid by uv spectroscopy. The band appeared at 330 nm.



14

Later, many studies have carried out on these species.[28-33] Well crystallized compounds of the dication of four sulfur atoms have been obtained by the following reactions (Scheme 13) and the salts were revealed to have the following structure (Figure 1), by Passmore *et al.*[31]

$$1/2\ S_8 + 3\ AsF_5 \xrightarrow[\text{trace } Br_2]{SO_2} S_4(AsF_6)_2{\bullet}xSO_2 + AsF_3$$

$$4\ S_8 + 2\ I_2 + 9\ AsF_5 \xrightarrow{SO_2} S_4(S_7I)_4(AsF_6)_6 + 3\ AsF_3$$

$$4\ S_8 + 2\ Br_2 + 9\ AsF_5 \longrightarrow S_4(S_7Br)_4(AsF_6)_6 + 3\ AsF_3$$

Scheme 13

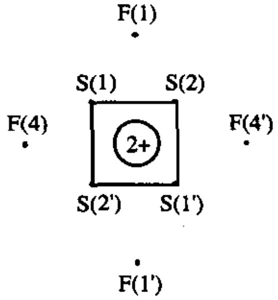


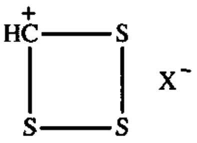
Figure 1 Structure of the S_4^{2+} cation in $S_4(AsF_6)_2{\bullet}0.62SO_2$ and nearest fluorine contacts from neighbouring AsF_6^- anions: S(1)–S(2), 2.015(3); S(1)–S(2'), 2.013(3); S(1)–F(1), 2.763(6); S(1)–F(4), 2.736(7); S(2)–F(1), 2.671; S(2)–F(4'), 2.664(6) Å; ∠S(2')S(1)S(2), 90.5(1); S(1)S(2)S(1'), 89.5(1)°

This is quite understandable, because the salts can obey Hückel's aromatic rule of $4n + 2$. Although the structure is square planar, the bond distances of S—S are all a bit shorter, perhaps because of the positive charge of sulfur atoms or the ring, however, the angles are nearly 90 °. While the bond order of S—S linkage is estimated as 1.25, the somewhat longer bond of S—S linkage despite of the double positive charges is believed to be due to the result of the repulsion of lone pairs on the sulfur atoms.

Similarly, $Se_4{}^{2+}$ and $Te_4{}^{2+}$ and also $Te_2Se_2{}^{2+}$ are also believed to be square planar polyatomic cations.[30,32] Molecular orbital scheme indicates that all these species are π-molecular structure and the molecules are square planar, however the uv bands are getting longer, i.e., 330 nm for $S_4{}^{2+}$, 410 nm for $Se_4{}^{2+}$, and 510 nm for $Te_4{}^{2+}$.[32]

How do these species behave in the chemical reaction ? This would be the interesting problem in the future.

If there would be a ring compound which has three sulfur atoms and one positively-charged carbon atom, shown in the structure (**15**), it would follow Hückel's rule of aromaticity and would exist as a semi-stable intermediate. However, no such a compound or its derivative has appeared up to now. Probably by replacing hydrogen by an aromatic group, such as phenyl or naphtyl group, one may obtain a rather stable salt, shown in the structure (**16**).



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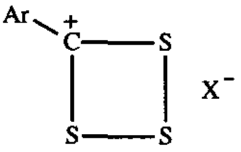

16

One can presume many interesting problems, such as various isomers of monosulfoxides, dioxides, and tetraoxides and others, however, none of these has been disclosed yet.

There are numerous studies about the chemistry of two sulfur atoms- and one sulfur atom-containing four-membered rings and these are so numerous that other reviews are neccessary.

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