

Computational study of base-induced skeletal conversion via a spirocyclic intermediate in dibenzodithiocinium derivatives by *ab initio* MO calculations

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ABSTRACT: Reaction of 6-methyl-12-oxo-5*H*,7*H*-dibenzo[*b,g*][1,5]dithiocinium salt (**1-SO**) with methanolic KOH afforded a mixture of dibenzothiepin derivatives **2-SO**. In order to clarify the intermediates of the rearrangement, *ab initio* MO calculations with the HF/6–31G* basis set were performed on the reaction intermediates, the transition states and related compounds. The rearrangement was explained in terms of the usual [2,3]-sigmatropic shift via a spirocyclic intermediate, followed by a 1,3-shift of the sulfonyl group. However, a different type of rearrangement was observed in 6-methyl-5*H*,7*H*-dibenzo[*b,g*][1,5]dithiocinium salt (**1-S**), giving an unexpected dibenzothiepin derivative **3-S** along with a small amount of a ring-opening product **8** under the same reaction conditions. The formation of **3-S** and **8** was understandable by the assumption of a cationic intermediate resulting from heterolytic cleavage at the benzyl position. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: Sommelet–Hauser rearrangement; dibenzo[*b,g*][1,5]dithiocinium salt; MO calculations; [2,3]-sigmatropic rearrangement

INTRODUCTION

The Sommelet–Hauser rearrangement is a very attractive reaction involving [2,3]-sigmatropic dearomatization followed by [1,3]-shift rearomatization processes,¹ by which the [2,3]-rearrangements of sulfonium ylides can be highly exothermic with low activation energies.² The Sommelet–Hauser rearrangement of 6-methyl-12-oxo-5*H*,7*H*-dibenzo[*b,g*][1,5]dithiocinium salt **1-SO** to **2-SO** was observed, and an interesting rearrangement via an alternative intermediate occurred in 6-methyl-5*H*,7*H*-dibenzo[*b,g*][1,5]dithiocinium salt **1-S** to produce **3-S** (Scheme 1).³ In this paper, we describe the computational study of these rearrangements by *ab initio* MO calculations with the HF/6–31G* basis set.

RESULTS AND DISCUSSION

Computational details

All the calculations were carried out at the Hartree–Hock (HF) level with the 6–31G* basis set using the program

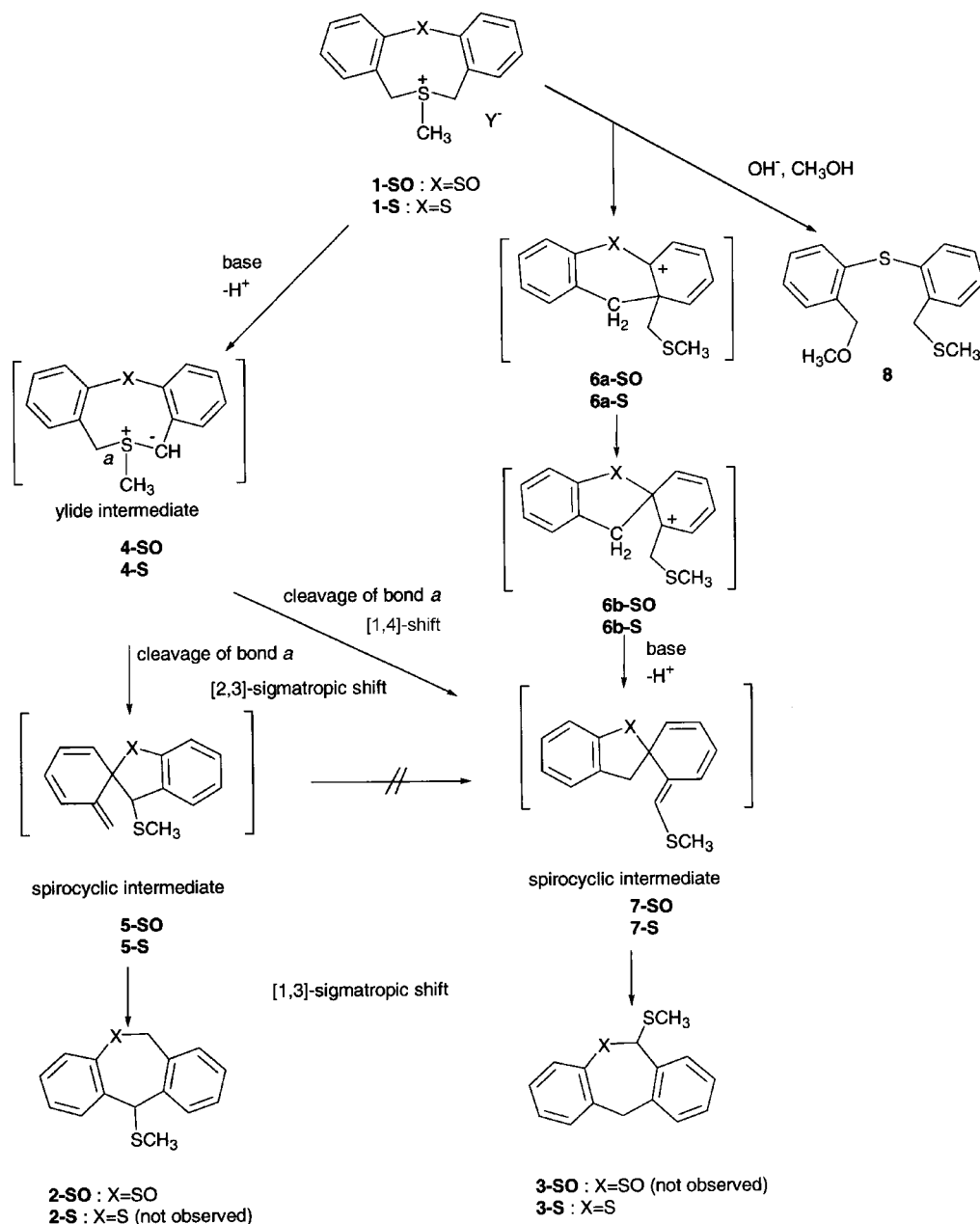
packages of HONDO2001.⁴ The calculations of transition structure search were carried out at the HF/6–31G* level using PC Spartan Pro (Wavefunction, Irvine, CA, USA). The initial geometries of the molecules were assumed by the PM3 method. Frequency calculations were carried out for the optimized geometries in order to verify that they were a minimum or a saddle point. All structures were optimized without geometric constraints.

Mechanistic consideration of the rearrangements

The rearrangement of **1-SO** into the dibenzothiepin derivatives in 66% yield was explained in terms of consecutive [2,3]- and [1,3]-sigmatropic shifts (the Sommelet–Hauser rearrangement) via a spirocyclic intermediate **5-SO** as shown in Scheme 1.

In this process from **1-SO** to **2-SO**, the sulfonium ylide **4-SO** was considered as the first generating intermediate.³ The anionic [2,3]-sigmatropic shift in **4-SO** gives spiro-**5-SO** by way of a concerted process (cleavage of bond *a*), followed by a [1,3]-shift to afford the final products **2-SO**. On the other hand, the other rearrangement of the sulfonium salt **1-S** into **3-S** was observed under the same reaction conditions. The rearranged product **3-S** in 29% yield along with a small amount of ring-opened product **8** could not be expected from such a Sommelet–Hauser type of rearrangement. Another inter-

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Scheme 1. The possible mechanism for the rearrangements of **1-SO** and **1-S**

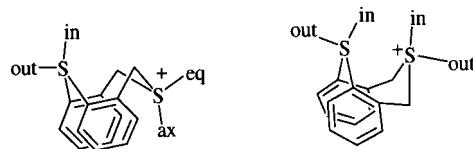
mediate such as spirocyclic intermediate **7-S** instead of **5-S** was assumed to explain the rearrangement of **1-S**. The difference in the rearrangement reaction in these ring systems is understandable in terms of the electronic factor rather than the steric factor.^{3b}

In the Sommelet–Hauser rearrangement, it is considered that the anionic carbon of the ylide **4-SO** attacks transannularly the *ipso* carbon in the aromatic ring, which is substituted by an electron-withdrawing group, in the sulfonium **1-SO**. On the other hand, the *ipso* carbon in the sulfonium **1-S**, substituted by an electron-donating group, is not reactive enough to be attacked intramolecularly by the anionic carbon of the ylide **4-S** as compared with that of **4-SO**. Hence an alternative [2,3]-sigmatropic shift of

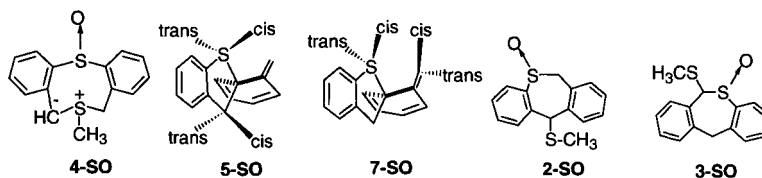
4-S can be considered to give the intermediate **7-S** ([1,4]-shift together with cleavage of bond *a*) or direct formation of cationic intermediate **6b-S** by way of a series of electrophilic attacks at the *ortho* carbon of the sulfinyl group to give **6a-S** and a 1,2-shift, followed by deprotonation to furnish the spirocyclic intermediate **7-S** as shown in Scheme 1. The formation of the ring-opening (benzyl carbon) product **8** supports the latter assumption.

MO calculation of reaction intermediates

We performed molecular orbital calculations on these various intermediates from the ylides **4** to the final

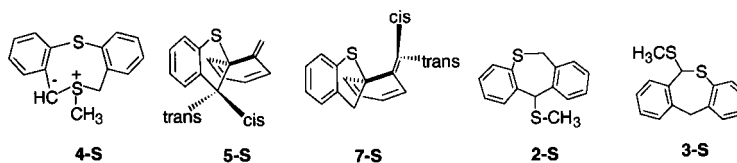
Table 1. Calculated total energies of the sulfonium ions **1-SO** and **1-S** and the relative energies from the most stable conformers **1-SO-cis-BC_e** and **1-S-BC_e**, respectively

Compound	SO	SCH ₃	Total energy (a.u.)	Relative energy (a.u.)	Relative energy (kJ mol ⁻¹)
1-SO-trans-BC_e	out	eq	-1446.344666	0.008713	22.88
1-SO-cis-BC_a	out	ax	-1446.344493	0.008885	23.33
1-SO-cis-BC_e	in	eq	-1446.353378	0 (std.)	0.0 (std.)
1-SO-trans-BC_a	in	ax	-1446.352229	0.001150	3.02
1-SO-trans-TB_i	out	in	-1446.335414	0.017965	47.17
1-SO-cis-TB_i	in	in	-1446.345348	0.008031	21.09
1-SO-cis-TB_o	out	out	-1446.334313	0.019065	50.06
1-SO-trans-TB_o	in	out	-1446.339658	0.013720	36.03
1-S-BC_a	—	ax	-1371.551260	0.003741	9.82
1-S-BC_e	—	eq	-1371.555002	0 (std.)	0.0 (std.)
1-S-TB_i	—	in	-1371.547783	0.007218	18.95
1-S-TB_o	—	out	-1371.548087	0.006914	18.16

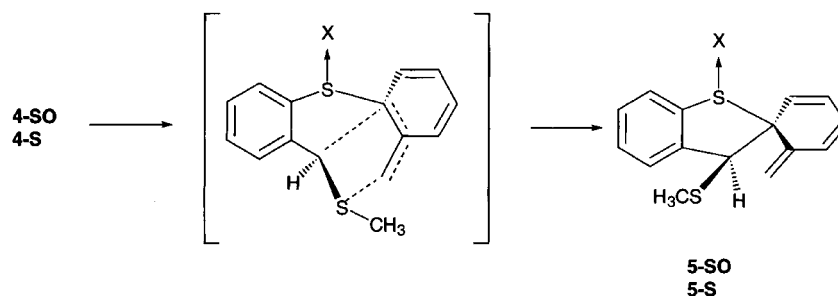
Table 2. Calculated total energy of the intermediates **4-SO**, **5-SO** and **7-SO** and the possible products **2-SO** and **3-SO** along with the relative energies with respect to **4-SO-cis-BC_e**

Compound	SO	SCH ₃	Total energy (a.u.)	Relative energy (a.u.)	Relative energy (kJ mol ⁻¹)
4-SO-trans-BC_a	<i>trans</i>	ax	-1445.891165	0.005593	14.69
4-SO-cis-BC_e	<i>cis</i>	eq	-1445.896758	0 (std.)	0.0 (std.)
4-SO-cis-BC_a	<i>cis</i>	ax	-1445.883497	0.013261	34.82
4-SO-trans-BC_e	<i>trans</i>	eq	-1445.885408	0.011350	29.80
4-SO-trans-TB_i	<i>trans</i>	in	-1445.875193	0.021564	56.62
4-SO-cis-TB_i	<i>cis</i>	in	— ^a	—	—
4-SO-cis-TB_o	<i>cis</i>	out	-1445.872324	0.024434	64.16
4-SO-trans-TB_o	<i>trans</i>	out	-1445.884548	0.012210	32.06
5-SO	<i>cis</i>	<i>cis</i>	-1445.938254	-0.041496	-108.96
	<i>cis</i>	<i>trans</i>	-1445.944893	-0.048136	-126.39
	<i>trans</i>	<i>trans</i>	-1445.942720	-0.045962	-120.68
7-SO	<i>trans</i>	<i>cis</i>	-1445.930751	-0.033993	-89.26
	<i>trans</i>	<i>trans</i>	-1445.948563	-0.051805	-136.03
	<i>cis</i>	<i>trans</i>	-1445.953492	-0.056735	-148.97
	<i>trans</i>	<i>cis</i>	-1445.946327	-0.049569	-130.15
2-SO	<i>cis</i>	<i>cis</i>	-1445.942507	-0.045749	-120.13
	<i>cis</i>	ax	-1445.991613	-0.094855	-249.06
	<i>cis</i>	eq	-1445.990224	-0.093466	-245.42
	<i>trans</i>	ax	-1445.989170	-0.092412	-242.65
3-SO	<i>trans</i>	eq	-1445.991557	-0.094799	-248.92
		<i>cis</i>	-1445.997794	-0.101036	-265.29
		<i>trans</i>	-1445.994768	-0.098010	-257.35
		<i>cis</i>	-1445.991791	-0.095033	-249.53
		<i>trans</i>	-1445.991338	-0.094581	-248.34

^a Not optimized.

Table 3. Calculated total energy of the intermediates **4-S**, **5-S** and **7-S** and the possible products **2-S** and **3-S** along with the relative energies with respect to **4-S-BC_a**

Compound	SCH ₃	Total energy (a.u.)	Relative energy (a.u.)	Relative energy (kJ mol ⁻¹)
4-S-BC_a	ax	-1371.092446	0 (std.)	0.0 (std.)
4-S-BC_e	eq	-1371.086938	0.005508	14.46
4-S-TB_i	in	-1371.085175	0.007272	19.09
4-S-TB_o	out	— ^a	—	—
5-S	<i>cis</i>	-1371.141552	-0.049105	-128.94
	<i>trans</i>	-1371.144447	-0.052000	-136.54
7-S	<i>trans</i>	-1371.149309	-0.056863	-149.31
	<i>cis</i>	-1371.147417	-0.054970	-144.34
2-S	ax	-1371.194839	-0.102393	-268.86
	eq	-1371.193415	-0.100969	-265.12
3-S	—	-1371.192353	-0.099907	-262.33
	—	-1371.192370	-0.099924	-262.37

^a Not optimized.**Scheme 2.****Table 4.** Relative energies of reaction intermediates

Compound	SO	SCH ₃	Total energy (a.u.)	Relative energy (a.u.)	Relative energy (kJ mol ⁻¹)
1-SO-TB	out	in	-1446.335414	0.000000	0.0
6a-SO	—	—	-1446.297664	0.037749	99.1
6b-SO	—	—	-1446.318311	0.017103	44.9
2-SO	<i>cis</i>	<i>exo</i>	-1445.990224	-0.117900	-309.5
3-SO	—	<i>cis</i>	-1445.997794	-0.125470	-329.4
4-SO	<i>exo</i>	<i>exo</i>	-1445.872324	0.000000	0.0
5-SO	<i>trans</i>	<i>cis</i>	-1445.930751	-0.058427	-153.4
7-SO	<i>trans</i>	<i>trans</i>	-1445.948563	-0.076239	-200.2
1-S-TB	—	in	-1371.547783	0.000000	0.0
6a-S	—	—	-1371.531470	0.016314	42.8
6b-S	—	—	-1371.520600	0.027184	71.4
2-S	—	<i>exo</i>	-1371.193415	-0.108241	-284.2
3-S	—	—	-1371.192353	-0.107179	-281.4
4-S	—	<i>endo</i>	-1371.085175	0.000000	0.0
5-S	—	<i>cis</i>	-1371.141552	-0.056377	-148.0
7-S	—	<i>trans</i>	-1371.149309	-0.064135	-168.4

Table 5. Activation energies of reaction A → B

A	B	ΔE^* (a.u.)	ΔE^* (kJ/mol ⁻¹)
4-SO	5-SO	0.027558	72.4
5-SO	2-SO	0.054917	144.2
7-SO	3-SO	0.053824	141.3
4-SO	7-SO	0.082214	215.9
1-S	6a-S	0.060461	158.7
6a-S	6b-S	0.044151	115.9
4-S	5-S	0.027752	72.9
5-S	2-S	0.065331	171.5
7-S	3-S	0.047725	125.3
4-S	7-S	0.068727	180.4

products **2** and **3** and related compounds to clarify these rearrangement reactions. For the *S*-methylthiociinium cations **1-SO-cis**, **1-SO-trans** and **1-S**, four stable conformations are capable of being populated. These are the BC_a and BC_e forms and the TB_i and TB_o forms, where the orientation of the methyl substituent on sulfur can be described as axial-like or equatorial-like in the BC forms (subscript a or e) and inside or outside in the TB forms (subscript i or o). Furthermore, we considered the geometric isomers in **1-SO** with respect to the MeS and SO groups where the position of the oxygen can be described as *cis* and *trans*, respectively. The BC conformation in which the CH₃S group attached at the

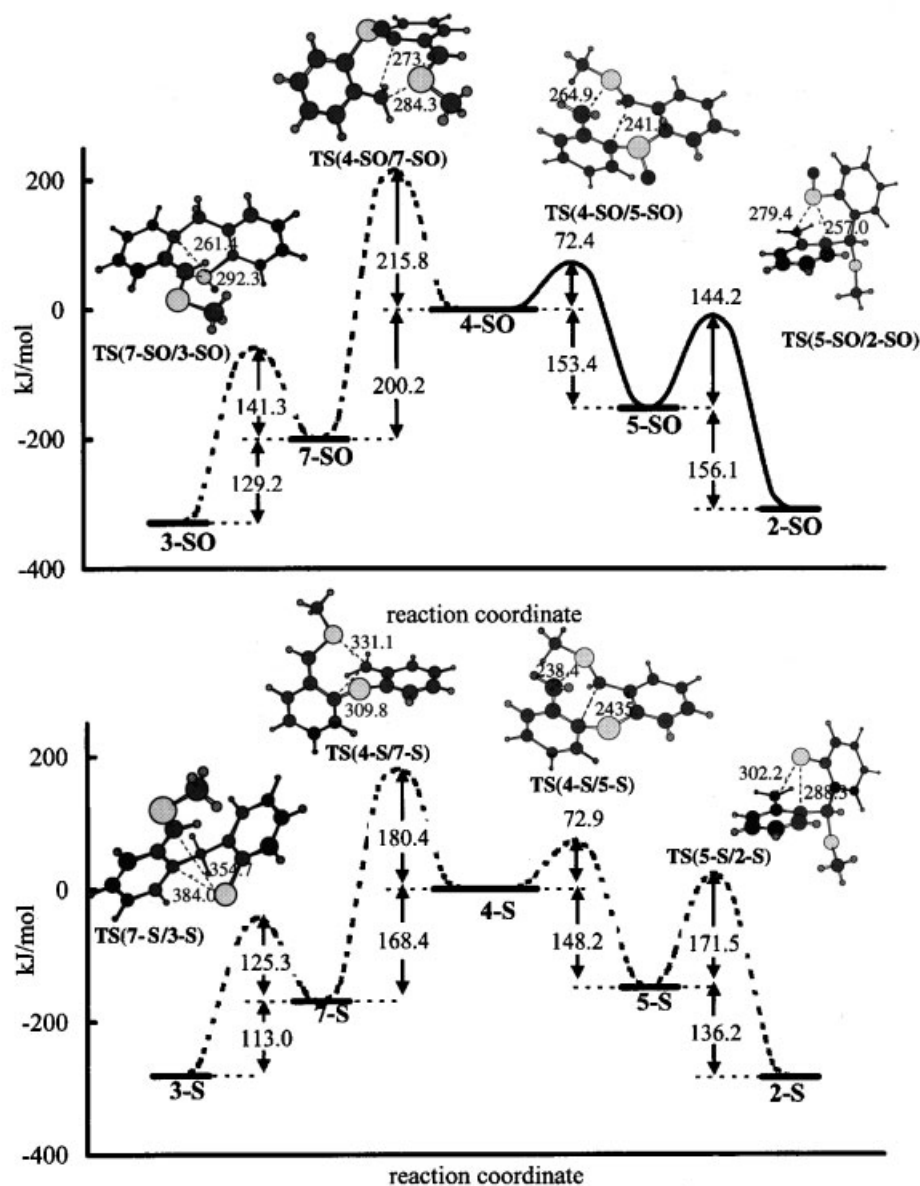


Figure 1. Reaction profiles in the rearrangements of **1-SO** (top) and **1-S** (bottom). Interatomic distances of the bond-forming and bond-fission sites in the transition states (TS) are given in pm

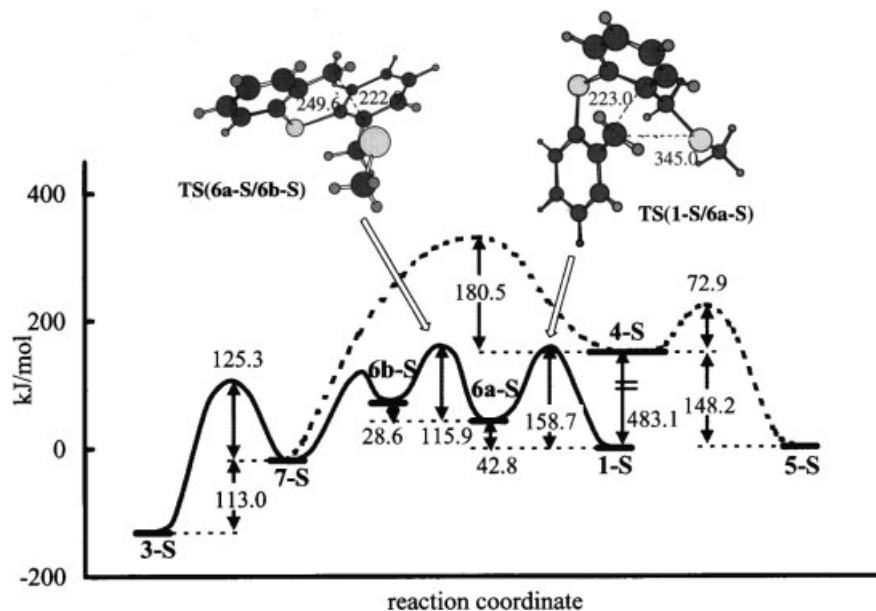


Figure 2. Direct reaction pathway from **1-S** to **7-S** via cationic intermediates **6a-S** and **6b-S**. Interatomic distances of the bond-forming and bond-fission sites in the transition states (**TS**) are given in pm

equatorial-like position of the eight-membered ring was the most stable in the starting materials, the sulfonium salts **1-SO** and **1-S**, as summarized in Table 1.

The spirocyclic intermediate **5-SO** gives the di-

benzothiocin derivatives **2-SO** after [1,3]-sigmatropic migration. This [1,3]-sigmatropic migration in the system involved aromatization to give dibenzo systems. As the constitutional elements of **4-SO**, **5-SO**, **7-SO**, **2-SO** and

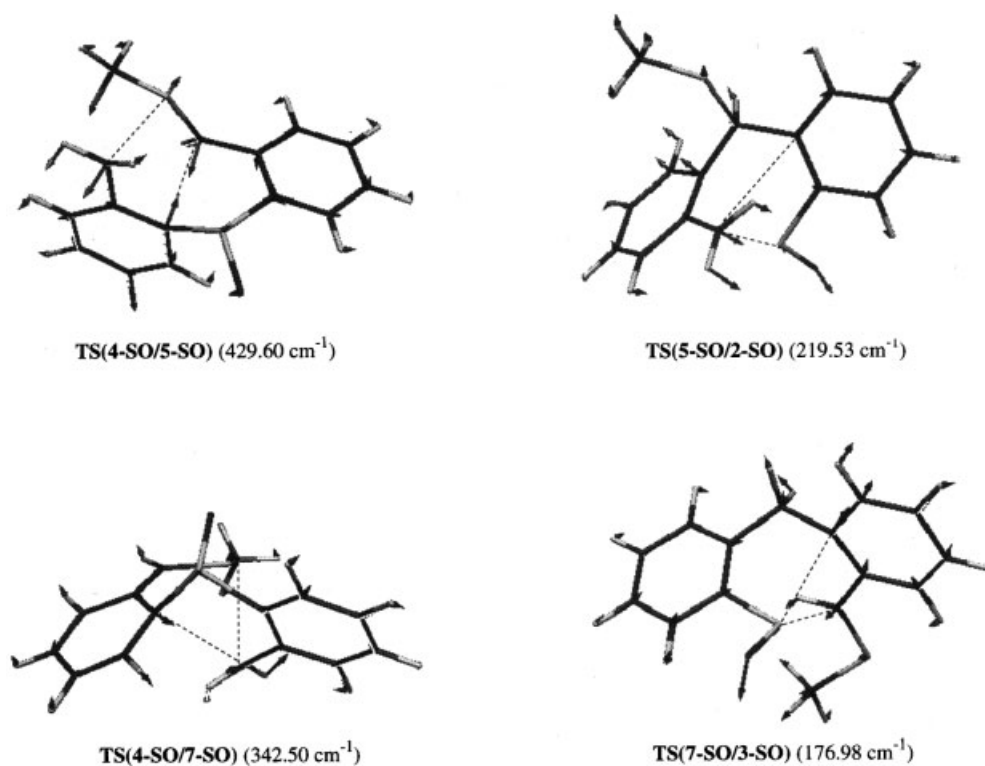


Figure 3. The reaction-coordinate vectors corresponding to the imaginary frequencies of the transition states related to the rearrangement of **1-SO**. The imaginary frequencies are shown in parentheses

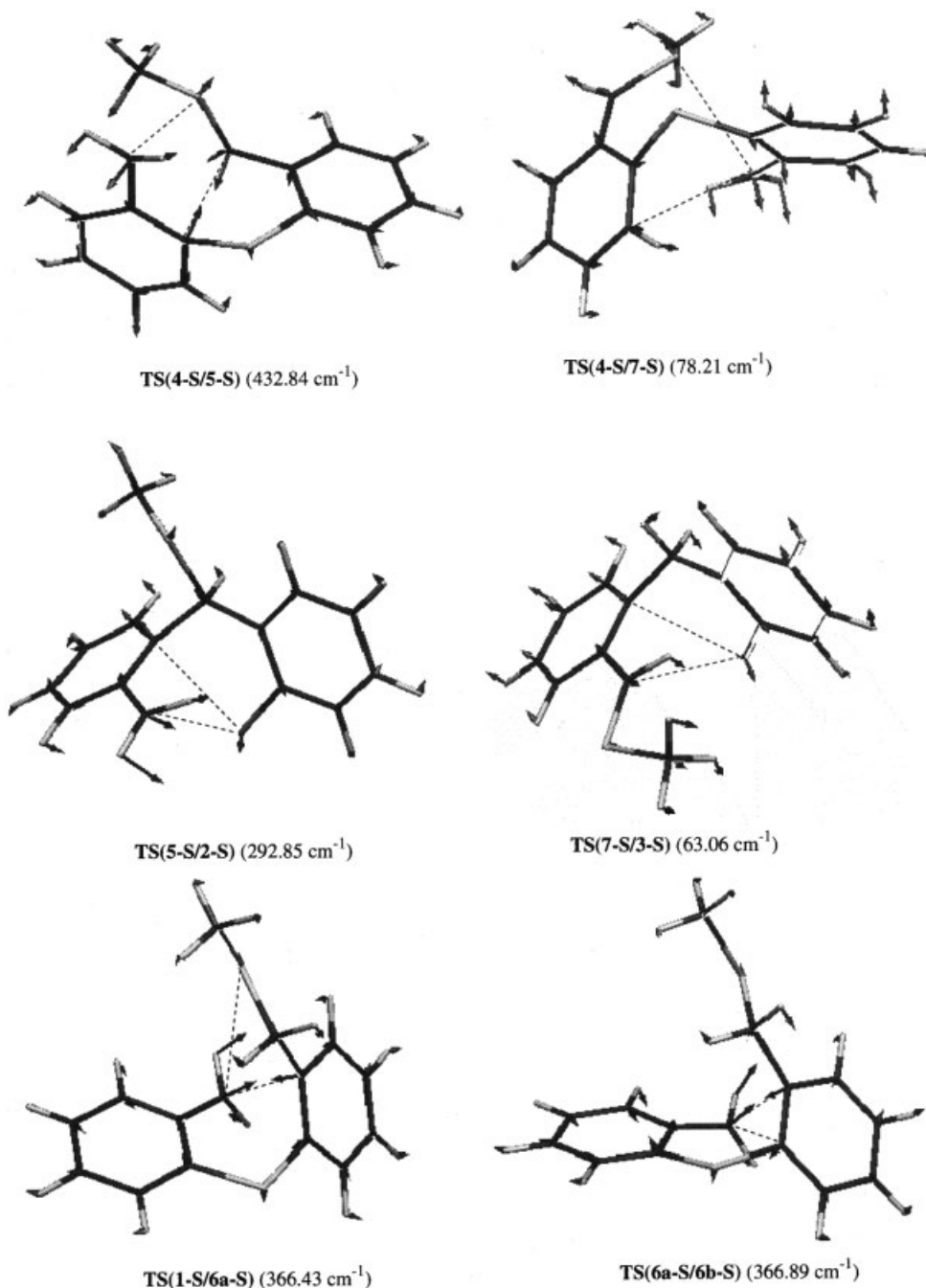


Figure 4. The reaction-coordinate vectors corresponding to the imaginary frequencies of the transition states related to the rearrangement of **1-S**. The imaginary frequencies are shown in parentheses

3-SO are similar to each other, it is possible to compare the energy levels of these compounds as summarized in Table 2.

Similar calculations were done in the rearrangement of the dithiocinium **1-S** (Table 3). In our previous speculation of the rearrangement mechanism, we assumed a mechanism via [3,3]-sigmatropic rearrangement from **5-S** into **7-S** to give **3-S**.^{3a} However, the structural rigidity in the ring system of **5-S** might restrict the [3,3]-sigmatropic rearrangement.⁵ Therefore, we can propose

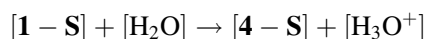
two other reaction paths, [2,3]-sigmatropic shift from **4-S** into **7-S** and direct formation of **7-S** via a heterolytic cleavage of the S—CH₂ bond in sulfonium **1-S** to give the final product **3-S**.

MO calculations of various transition states and consideration of reaction profile

According to the principle of least motion,⁶ spirocyclic

intermediates **5** in which the methylsulfenyl and sulfinyl groups are *cis* to the *exo*-methylene group with respect to the dihydrothiophen ring after [2,3]-sigmatropic rearrangement of the ylides **4** are considered. Flexibility of the ylide ring system is necessary for the first-step [2,3]-rearrangement to proceed. Therefore, the [2,3]-rearrangement is thought to proceed from the TB_i form of the ylide to *cis*-methylsulfenyl spirocyclic intermediates as shown in Scheme 2.

When these rearrangements proceed via the ylide intermediate, it is presumed that the intermediates and reaction products are **4-SO-*cis*-TB_o**, **5-SO** (SO/SMe = *trans/cis*), **7-SO** (SO/SMe = *trans/trans*), **2-SO** (SO/SMe = *cis/eq*) and **3-SO** (SMe = *cis*) for the **1-SO** series, and **4-S-TB_o**, **5-S** (SMe = *cis*), **7-S** (SMe = *trans*), **2-S** (SMe = *eq*) and **3-S** for the **1-S** series. The relative energies based on the sulfonium species and the ylides are shown in Table 4. The activation energies (ΔE^*) in each reaction from A to B are shown in Table 5. In order to compare with the energy levels of the sulfonium salt **1-S** and the ylide **4-S**, the potential energy values of H₂O (−76.01075 a.u.) or H₃O⁺ (−76.28934 a.u.) were added to the corresponding energy values to make the isodesmic reaction



In the isodesmic reaction, the ylide system is expected to be 483.1 kJ mol^{−1} less stable than the sulfonium system. Thus, the activation energy of rearrangement from **1-S** to **3-S** via the ylide is 397.7 kJ mol^{−1} higher than that of **1-S** via **6a** by way of the cationic fission of the sulfoxide (from **7-SO** to **3-SO**) without consideration of the solvent effect.

The relationship of the energy levels between the intermediates for the rearrangements and activation energies are shown schematically in Fig. 1. The transition structures along the interatomic distances in the bond-forming and bond-fission sites are illustrated in Figs 1 and 2. The transition states for each rearrangement have been optimized at the HF/6–31G* level. These are characterized by imaginary frequencies as shown in Figs 3 and 4.

As displayed in Figs 3 and 4, the reaction-coordinate vectors of the corresponding transition states indicate the bond fission and bond formation in the reaction sites. There are several interesting points in Fig. 1. In the rearrangement from **4-SO** into **2-SO** the decrease in energy level for the first step ([2,3]-sigmatropic shift) was about 89–144 kJ mol^{−1} and the second step ([1,3]-sigmatropic shift) was stabilized by about 130–160 kJ mol^{−1} (Table 2). It seems that the driving force of the first step is caused by the conversion of the unstable ylide into the spirocyclic intermediate in spite of the dearomatization, followed by the second step of rear-

omatization to give the final product **2-SO**. The first steps from **4** into **5** and **7** in both rearrangements are the rate-determining step in the formation of **2** and **3**, respectively. Judging from the activation energies, conversion from **4-SO** to **5-SO** is smoother than that from **4-SO** to **7-SO**. Although the process from **4-S** to **5-S** is more favorable than that to **7-S** according to the calculations, the expected product **2-S** was not observed in the rearrangement.

The activation energy of the final [1,3]-sigmatropic rearrangement from the sulfoxide **5-SO** to **2-SO** is 27 kJ mol^{−1} lower than that of the sulfide (from **5-S** to **2-S**). On the other hand, the activation energy of the final [1,3]-sigmatropic rearrangement from the sulfide **7-S** to **3-S** is 16 kJ mol^{−1} lower than that of the sulfoxide (from **7-SO** to **3-SO**).

The rearrangement of sulfoxide **1-SO** into **2-SO** is understandable in terms of the above reaction profile, while the rearrangement of sulfide **1-S** into **3-S** cannot be explained by the above reaction profile. Therefore, the direct pathway from **1-S** to **7-S**, not via the ylide **4-S**, was suggested, as shown in Fig. 2. Furthermore, it is considered that the transition state in the consecutive cationic reaction from **1-S** to **6b-S** (ionic mechanism) is more stabilized in polar solvents such as an alcohol as compared with the solvent effect of the rearrangement (concerted mechanism) from **4-S** to **7-S** and **4-S** to **5-S**.

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