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Rearrangement of 6,7-Dithiabicyclo[3.1.1]heptane 6-Oxides to a 7,8-Dithia-6-oxabicyclo[3.2.1]octane Catalyzed by Montmorillonite K 10

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ABSTRACT

*Treatment of 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane 6-endo-oxide (**2**) with Montmorillonite K 10 in dichloromethane gave 2,2,-4,4-tetramethyl-1,5-diphenyl-7,8-dithia-6-oxabicyclo-[3.2.1]octane (**6**) (11%) with recovery of **2** (87%). Under similar reaction conditions, the 6-exo-oxide **7** and the sulfenate **6** gave a mixture of **6** (21%), **2** (67%), and **7** (9%) and a mixture of **2** (89%) and **6** (9%), respectively. These results indicate the relative thermodynamic stabilities of the three compounds to be **2** > **6** > **7**. PM3 calculations on these compounds showed the heats of formation (kcal/mol) to be in the following order: **6** (44.12783), **2** (57.46721), and **7** (59.37918). The driving force of this unusual 1,2-rearrangement of **2** and **7** to **6** would be the release of the ring strain of the bicyclo[3.1.1]heptane system of **2** and **7** by ring expansion.*

INTRODUCTION

Recently, we reported the first isolation of a dithiirane *S*-oxide derivative **1** by the reaction of 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo-[3.1.1]heptane 6-*endo*-oxide (**2**) with $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (OXONE, Aldrich) in a two-phase mixture of dichloromethane and water in the presence of a phase-transfer catalyst [1]. Later, we also succeeded in the isolation of unoxidized dithiirane **3** by the reaction of 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane (**4**) with OXONE under similar reaction conditions [2]. These reactions proceeded only under acidic conditions and can be regarded as examples of an oxidative hydrolysis of a dithioacetal under acidic conditions. In the course of our investigation to seek another route to **1** from **2**, we examined the reaction of **2** with *t*-butyl hydroperoxide (*t*-BuOOH) as an oxidant in the presence of Montmorillonite K 10 as a catalyst. Montmorillonite K 10 and ion-exchanged Montmorillonites are acidic clays and have been applied to organic syntheses as acid catalysts [3]. The reaction unexpectedly yielded 2,2,4,4-tetramethyl-1, 5-diphenyl-7, 8 -dithia -6-oxabicyclo[3.2.1]-octane 7-oxide (**5**) in 10% yield (Equation 1). This result suggests the occurrence of a 1,2-rearrangement of the sulfoxide group of **2** to give the corresponding sulfenate **6**, followed by oxidation to **5**. While the 2,3-sigmatropic rearrangement of sulfoxides to sulfenates has been widely utilized in organic syntheses [4], there have appeared only a few reports of the 1,2-rearrangement of sulfoxides to sulfenates. For example, thermal 1,2-rearrangements of methoxymethyl [5] and benzyloxymethyl [6] phenyl sulfoxides to the corresponding sulfenates have been reported, where an intramolecular rearrangement was proposed for the former rearrangement and, on the other hand, a bimolecular oxygen-transfer mechanism for the latter. Photo-

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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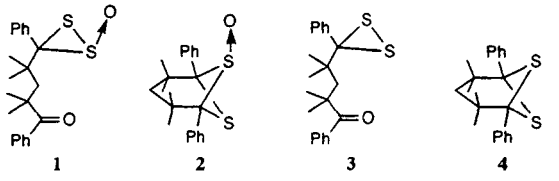
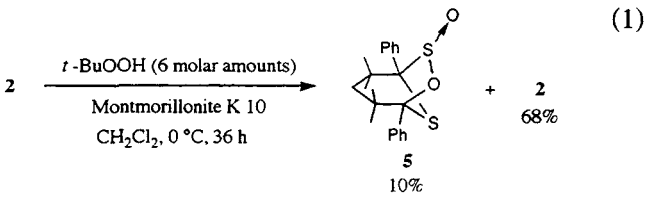
chemical 1,2-rearrangements of sulfoxides to sulfenates, which are initiated by the homolytic cleavage of C(benzyl)–S bonds, have also been reported [7,8]. Furthermore, it was reported that alkyl benzenesulfenates readily isomerize to the corresponding sulfoxides by treatment with acid [9]. In this article, we report an unprecedented type of interconversion between *endo*-sulfoxide **2**, *exo*-sulfoxide **7**, and cyclic sulfenate **6** and also results of PM3 calculations on these compounds.



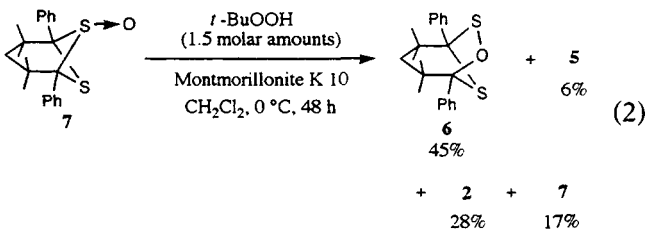
1 **2** **3** **4**



(1)

RESULTS AND DISCUSSION

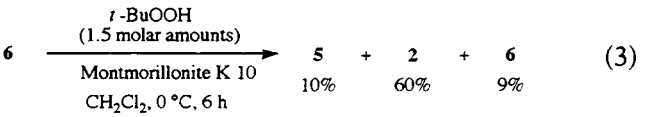
The reaction of **2** with *t*-BuOOH was so sluggish that a sixfold molar amount of *t*-BuOOH was used, in total, in the reaction depicted in Equation 1. On the other hand, when *exo*-sulfoxide **7** was allowed to react with a 1.5 molar amount of *t*-BuOOH (70%) in the presence of Montmorillonite K 10 in dichloromethane at 0°C, sulfenate **6** (45%), sulfinate **5** (6%), and *endo*-sulfoxide **2** (28%) were isolated, along with recovery of **7** (17%) (Equation 2).



(2)

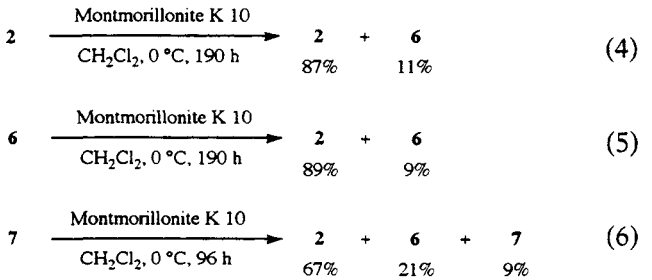
The structure of sulfenate **6** was determined by analysis of its spectroscopic data and elemental analysis. In the ^1H and ^{13}C NMR spectra, four methyls as well as two phenyls and two methylene protons are unequivalent. In addition, in the ^{13}C NMR spectrum, two quaternary carbons assignable to bridgehead carbons appear at δ 86.38 and 112.97. No carbonyl carbon is observed. These observations indicate that **6** has a 7,8-dithia-6-oxabicyclo[3.2.1]octane skeleton, which is a sulfur analog of cyclopentene ozonide [10,11].

On the other hand, the structure of sulfinate **5** was elucidated as follows. The unsymmetric, bicyclic structure, similar to **6**, was supported by the ^1H NMR spectrum. In the IR spectrum, an absorption due to the sulfinate group is observed at 1152 cm^{-1}. In the mass spectrum, the largest peak is not due to the molecular ion (M^+) but due to the ion assigned to M^+-SO_2. In addition, oxidation of sulfenate **6** with *t*-BuOOH in the presence of Montmorillonite K 10 in dichloromethane at 0°C yielded **5** in 10% yield, with concomitant isomerization of **6** to *endo*-suloxide **2** (Equation 3). Thus, we assigned the structure of **5** as shown, although the configuration about the sulfur atom was not determined.



(3)

It is apparent from Equations 1 through 3 that the isomerization of sulfoxides **2** and **7** to sulfenate **6** occurred first and then **6** was oxidized to sulfinate **5**. Therefore, we next investigated the Montmorillonite K 10 catalyzed interconversion between **2**, **6**, and **7**. Thus, Montmorillonite K 10 was suspended in a solution of **2** in dichloromethane, and the mixture was stirred at 0°C for 190 hours to give rise to sulfenate **6** in 11% yield along with the recovery of **2** (87%) (Equation 4). Under similar conditions, 89% of sulfenate **6** isomerized to *endo*-sulfoxide **2** (Equation 5). When a solution of *exo*-sulfoxide **7** in dichloromethane was stirred with Montmorillonite K 10 for a shorter period (96 hours), **6** (21%), **2** (67%), and **7** (9%) were obtained (Equation 6). These results lead to the conclusion that the order of thermodynamic stabilities of these three compounds is **2** > **6** ≫ **7**.



(4)

(5)

(6)

Although the relative stabilities of **2** and **7** were predictable from our previous observation on the facile isomerization of 2,2,3,3-tetramethyl-1,4-diphenyl-5,6-dithiabicyclo[2.1.1]hexane 5-*exo*-oxide (**8**) to the corresponding 5-*endo*-oxide **9** (Equation 7) [12], the isomerization of sulfoxides **2** and **7** to sulfenate **6** is of particular interest. Analogous heterocycles, 2,3-dimethyl-5,6-dithiabicyclo[2.1.1]-hexane 5-oxides (**10** and **11**) and 5,6-dimethyl-2,7-

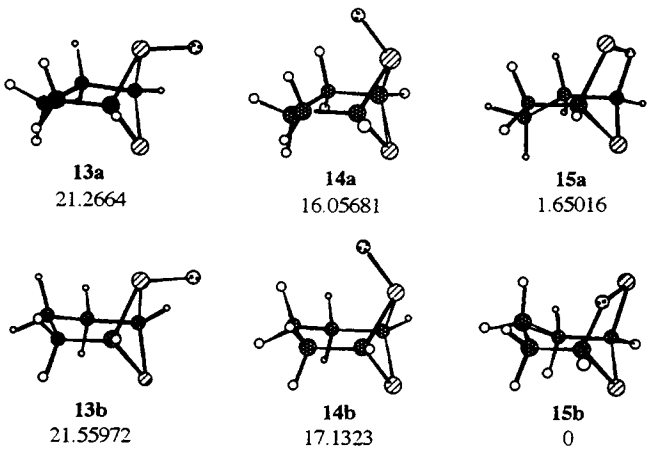


FIGURE 1 Optimized structures and differences of calculated heats of formation (kcal/mol) by PM3 calculations.

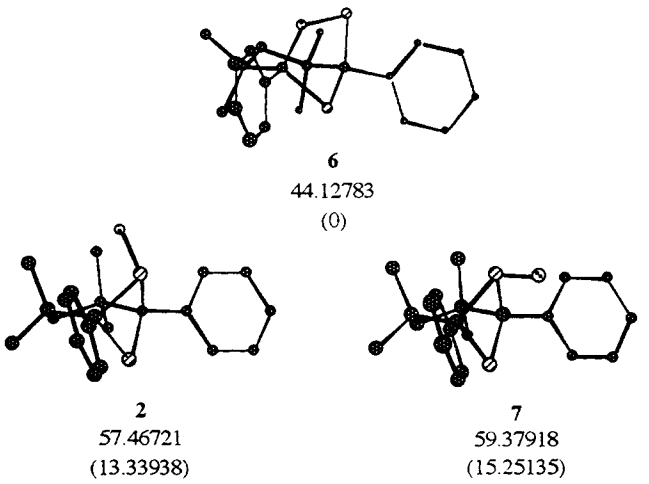
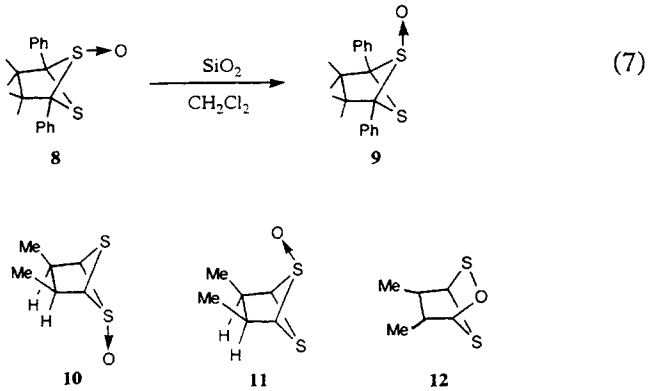


FIGURE 2 Optimized structures (hydrogen atoms are omitted) and calculated heats of formation (kcal/mol) by PM3 calculations. Difference of energy is presented in parentheses.

dithia-3-oxabicyclo[2.2.1]heptane (**12**), have been isolated from onion, and the possibility of the isomerization of **12** to **10** or **11** was suggested [13]. To consider the relative stabilities of **2**, **6**, and **7** from a theoretical standpoint, we have carried out PM3 calculations [14]. Prior to calculations on **2**, **6**, and **7**, values of the heats of formation of two isomers (**13** and **14**) of unsubstituted 6,7-dithiabicyclo[3.1.1]heptane 6-oxide and of 7,8-dithia-6-oxabicyclo[3.2.1]octane (**15**) were calculated. For each compound, two conformers were taken into account. The results are summarized in Figure 1. With regard to conformers **13a** and **14a**, chair forms inclusive of C(3) and S(6) are more stable than the corresponding boat forms depicted in **13b** and **14b**, respectively, but the boat conformer of the seven-membered ring **15b** is more stable than the chair conformer **15a**. Among the three structural isomers, the most stable one is the sulfenate **15**, followed by sulfoxides **14** and **13** in that order. Calculations on **2**, **6**, and **7** were carried out on the corresponding conformers that were shown to be more stable in their unsubstituted molecules. The order of their relative stabilities is sulfenate **6** ≫ *endo*-sulfoxide **2** > *exo*-sulfoxide **7**, as presented in Figure 2.

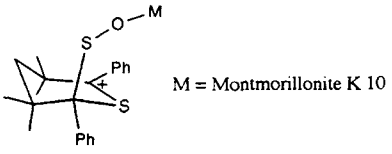


(7)

In both cases, PM3 calculations showed that sulfenates **6** and **15** are more stable than sulfoxides **2** and **7** and **13** and **14**, respectively. The larger stability of **6** relative to **2** and **7** is not in harmony with the experimental results. Wolfe and Schlegel reported ab initio calculations on dimethyl sulfoxide [MeS(=O)Me] and methyl methanesulfenate (MeSOMe) [15]. The calculated heat of reaction for the process MeSOMe → MeS(=O)Me at the HF/6-31G(d) level is 11.30 kcal/mol endoergic, indicating that MeSOMe is thermodynamically more stable than MeS(=O)Me. Similar larger stabilities of sulfenate tautomers than sulfoxide ones are shown in the calculations of the processes HSOH → HS(=O)H, MeSOH → MeS(=O)H, and HSOMe → HS(=O)Me. However, the calculated dimerization energy of MeS(=O)Me is 16.82 kcal/mol, and, on the other hand, that of MeSOMe is only 1.29 kcal/mol. This large dimerization energy of MeS(=O)Me explains the reason why dimethyl sulfoxide exists as the sulfoxide form predominantly in condensed phases.

Similar considerations may hold also for the present case. Thus, *endo*-sulfoxide **2** would be stabilized by forming a dimeric (or oligomeric) form and would also be solvated to a considerably larger extent than **6**, which rationalizes the discrepancy between the calculations and the experimental results. However, the steric hindrance around the sulfoxide group of **2** might decrease such stabilization effects. Moreover, the large ring strain residing inherently in the bicyclo[3.1.1]heptane ring of **2** would enable a plausible intermediate **16** to recyclize to **6** and permit the existence of **6** in the equilibrium mixture. Incidentally, the rearrangements of **2** and **7** to **6** were not observed when they were treated with protic acids like $KHSO_4$. In ad-

dition, **2**, **6**, and **7** were not oxidized with *t*-BuOOH in the absence of Montmorillonite K 10 at 0°C. Therefore, Montmorillonite K 10 catalyzes both rearrangement and oxidation reactions.



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EXPERIMENTAL

General Procedures

Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H NMR spectra were determined at 400 MHz and ^{13}C NMR spectra at 100.6 MHz using $CDCl_3$ as the solvent on a Bruker AM-400 spectrometer. Mass spectra were obtained at 70 eV in the EI mode on a Shimadzu QP-1000 spectrometer and IR spectra on a Hitachi Model 270-50 spectrometer. Elemental analyses were performed by the Analytical Center of Saitama University.

Both *endo*- and *exo*-sulfoxides **2** and **7** were prepared by oxidation of 2,2,4,4-tetramethyl-1,5-diphenyl-6,7-dithiabicyclo[3.1.1]heptane (**4**) [16] with *m*-chloroperbenzoic acid [1]. Montmorillonite K 10 and *t*-BuOOH (70%) were purchased from Aldrich Co. (Milwaukee, WI) and used as such.

Oxidation of **2** *with t-BuOOH in the Presence of Montmorillonite K 10.* To a solution of **2** (105.2 mg, 0.296 mmol) in dichloromethane (20 mL) were added Montmorillonite K 10 (0.5 g) and *t*-BuOOH (70%, 57 mg, 0.44 mmol) at 0°C. The mixture was stirred at 0°C for 36 hours, while another amount of *t*-BuOOH was added after 13 and 24 hours (57 mg and 114 mg, respectively) since the reaction was sluggish. Montmorillonite K 10 was removed by filtration, and the filtrate was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give **2** (71.5 mg, 68%) and sulfinate **5** (10.8 mg, 10%), mp 175–180°C decomp (from hexane); results by ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.68 (s, 3H), 1.22 (s, 3H), 1.29 (s, 3H), 1.40 (s, 3H), 1.46 (d, J = 15 Hz, 1H), 1.77 (d, J = 15 Hz, 1H), 7.29–7.36 (m, 8H), 7.53–7.55 (m, 2H); by IR (KBr) 2968, 2920, 1446, 1152, 866, 766, 730, 696 cm^{-1}; by MS, m/z 308 (M^+–SO_2), 293, 261.

Oxidation of **7** *with t-BuOOH in the Presence of Montmorillonite K 10.* To a solution of **7** (590.4 mg, 1.66 mmol) in dichloromethane (70 mL) were added Montmorillonite K 10 (0.5 g) and *t*-BuOOH (70%, 321 mg, 2.49 mmol) at 0°C. The mixture was stirred at 0°C for 48 hours. Montmorillonite K 10 was removed by filtration, and the filtrate was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to elute sulfenate **6** (262.8 mg, 45%), *endo*-sulfoxide **2** (163.4 mg, 28%), sulfinate **5** (38 mg, 6%), and **7** (100.3 mg, 17%) in this order. **6**, pale yellow needles, mp 202–207°C decomp (from hexane); results by ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85 (s, 3H), 1.05 (s, 3H), 1.33 (s, 3H), 1.35 (d, J = 14.5 Hz, 1H), 1.43 (s, 3H), 2.19 (d, J = 14.5 Hz), 7.12–7.14 (m, 2H), 7.26–7.33 (m, 6H), 7.48–7.51 (m, 2H); by ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.95 (CH_3), 27.12 (CH_3), 27.51 (CH_3), 29.44 (CH_3), 42.74 (C), 43.82 (C), 52.16 (CH_2), 86.38 (C), 112.97 (C), 127.35 (CH), 127.53 (CH), 127.59 (CH), 127.63 (CH), 128.29 (CH), 128.61 (CH), 135.49 (C), 139.07 (C); by IR (KBr) 2962, 2920, 1449, 915, 891, 777, 735, 696 cm^{-1}; by MS m/z 356 (M^+), 308, 293. Anal. calcd for $C_{21}H_{24}OS_2$: C, 70.74; H, 6.78; found: C, 70.96; H, 6.80.

Oxidation of Sulfenate **6** *with t-BuOOH in the Presence of Montmorillonite K 10.* To a solution of **6** (26.9 mg, 0.0759 mmol) in dichloromethane (20 mL) were added Montmorillonite K 10 (0.3 g) and *t*-BuOOH (70%, 21 mg, 0.11 mmol) at 0°C. The mixture was stirred at 0°C for 6 hours, and Montmorillonite K 10 was removed by filtration. The filtrate was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give sulfenate **6** (2.4 mg, 9%), *endo*-sulfoxide **2** (15.2 mg, 60%), and sulfinate **5** (7.0 mg, 10%).

Isomerization of endo-Sulfoxide **2** *Catalyzed by Montmorillonite K 10.* Montmorillonite K 10 (0.5 g) was added to a solution of **2** (352.3 mg, 0.988 mmol) in dichloromethane (25 mL), and the suspension was stirred at 0°C. After 190 hours, Montmorillonite K 10 was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give sulfenate **6** (38.2 mg, 11%) and **2** (303.2 mg, 86%).

Isomerization of Sulfenate **6** *Catalyzed by Montmorillonite K 10.* Montmorillonite K 10 (0.3 g) was added to a solution of **6** (42.1 mg, 0.118 mmol) in dichloromethane (20 mL), and the suspension was stirred at 0°C for 190 hours. Montmorillonite K 10 was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to provide **6** (3.8 mg, 9%) and **2** (37.4 mg, 89%).

Isomerization of exo-Sulfoxide **7** *Catalyzed by Montmorillonite K 10.* Montmorillonite K 10 (0.5

g) was suspended in a solution of **7** (127 mg, 0.358 mmol) in dichloromethane (30 mL), and the mixture was stirred at 0°C for 96 hours. Montmorillonite K 10 was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2) to give sulfenate **6** (26.4 mg, 21%), *endo*-sulfoxide **2** (85.1 mg, 67%), and **7** (11.7 mg, 9%).

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