Methyl Sulfonium Salts of 9,9'-Bibenzonorbornenylidene Episulfides: Preparation and Isomerization

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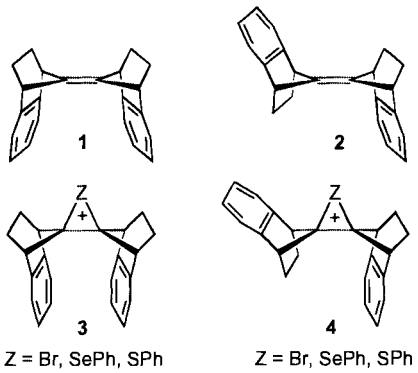
Methylations of bibenzonorbornenylidene episulfides **5** and **6** by $Me_3O^+BF_4^-$ at –18 °C furnished the corresponding episulfonium salts **7** and **8**, respectively, with retention of the configuration of the episulfides, whereas those at room temperature or above produced a mixture of **7** and **8** in the ratio of about 1:4. Dynamic ^1H NMR investigation in the temperature range 25–40 °C allowed the determination of the activation parameters of the isomerization between **7** and **8**, which obeyed first-order kinetics.

We have been investigating the synthesis, structure, and reactivities of *syn*- and *anti*-9,9'-bibenzonorbornenylidenes **1** and **2**[1] and their derivatives. The stereochemistry of the reactions of **1** and **2** is of particular interest because the benzonorbornenylidene group exerts not only steric effects by its bulkiness but also anchimeric assistance by the benzene ring.[2] The reactions of these alkenes are classified into two categories. Thus, sulfurations with elemental sulfur,[3] which belong to the first category, afford episulfides with retention of the configuration of the starting alkenes. The second one includes the reactions with halogens[4] and with PhSeCl and PhSCl,[5] where the configuration of the alkene is retained in the case of **1**, whereas, in marked contrast, the configuration of the alkene is inverted in the case of **2** to produce the same adduct as that from **1**. In the reactions of the second category, the onium salts **3** and **4** would be involved as the key intermediates.[6] Therefore, in order to understand the stereochemisry of the reactions of **1** and **2** and their derivatives, study of these onium salts is of crucial importance. We report here the preparation of the methyl sulfonium salts of bibenzonorbornenylidene episulfides and their isomerization.



Results of methylations of the *syn*- and *anti*-episulfides, **5** and **6**, by $Me_3O^+BF_4^-$ in CH_2Cl_2 are summarized in Table 1. The methylation of **5** by 1 equiv of $Me_3O^+BF_4^-$ at –18 °C for 55 days gave *syn*- and *anti*-episulfonium salts **7** and **8** in 60 and 6% yields, respectively, with 32% recovery of **5** (entry 1).[7–9] The methylation of **6** at the same temperature for 8 days furnished **7** and **8** in 1 and 46% yields, respectively, with 47% recovery of **6**. In the ^{13}C NMR spectra at –20 °C, **7** showed five sp^3 carbon peaks because of accidental overlapping of the two peaks, in addition to six aromatic carbon peaks, while **8** showed eleven sp^3 carbon peaks in addition to twelve aromatic carbon peaks.[8] In the ^1H NMR spectra, the methyl hydrogen signal of **8** appeared at a higher field than that of **7** and, in addition, the aromatic hydrogen signals of **7** appeared at higher fields than those of **8**.[8] The above high field shifts in **7** are explained as a result of the ring-current effect of the benzene rings, which are placed in a face-to-face orientation.[1,3,4] The steric hindrance caused by the two ethylene bridges would be responsible for the slower methylation of **5** than that of **6**.

The methylation of **5** at room temperature for 6 days gave **7** and **8** in 14 and 56% yields (entry 3), respectively, while that

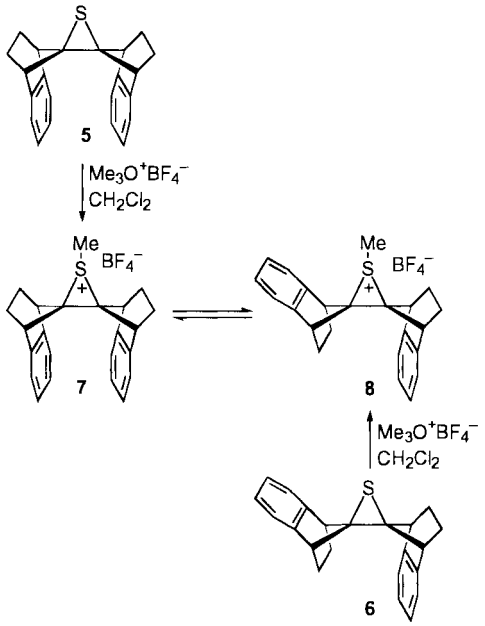


Table 1. Methylations of Episulfides with 1 equiv of $Me_3O^+BF_4^-$ in CH_2Cl_2

Entry	Episulfide	Temp./°C	Time	Products (Yield/%)
1	**5**	–18	55 d	**7** (60), **8** (6), **5** (32)
2	**6**	–18	8 d	**7** (1), **8** (46), **6** (47)
3	**5**	RT[a]	6 d	**7** (14), **8** (56)
4	**5**	reflux	3 h	**7** (18), **8** (71)
5	**6**	RT[a]	6 d	**7** (17), **8** (68)
6	**6**	reflux	3 h	**7** (18), **8** (72)

[a] RT stands for room temperature.

of **6** under the same conditions gave **7** and **8** in 17 and 68% yields, respectively (entry 5). The methylations of **5** and **6** at refluxing temperature provided **7** and **8** essentially in the same ratios as those at room temperature (entries 4 and 6).

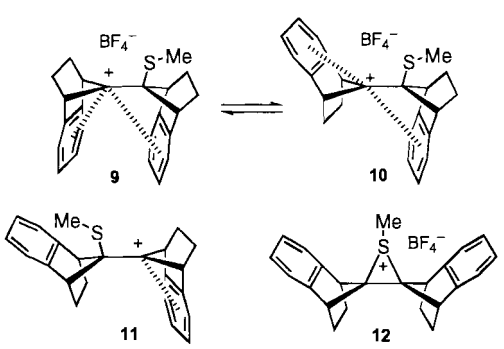
These observations lead to the conclusions that 1) the methylations of **5** and **6** at –18 °C principally produce the sulfonium salts **7** and **8**, respectively, in which the original stereochemistry of the episulfide is retained and 2) the mutual isomerization between **7** and **8** takes place at room temperature or above and probably reaches an equilibrium under the applied conditions.[10] Indeed, the dynamic ^{1}H NMR measurements of **7** from at –10 to 40 °C revealed that the signal intensities of **7** decreased with increasing signal intensities of **8** on rising temperature. Any signals that would be ascribable to the intermediates of the isomerization were not observed during the measurements.

The progression of the isomerization of **7** to **8** was then followed by ^{1}H NMR in the temperature range 25–40 °C. In a 4.8 mM $CDCl_3$ solution, the isomerization between **7** and **8** obeyed first-order kinetics. The rate constants for the isomerization of **7** to **8** were (2.16, 5.10, 7.16, and 21.2) $\times 10^{-5}$ s^{-1} and those of **8** to **7** were (0.51, 1.20, 1.79, and 4.99) $\times 10^{-5}$ s^{-1} at 25, 30, 35, and 40 °C, respectively. The final equilibrium ratio of **7** to **8** was about 1:4 at 25–40 °C. The kinetics led to the activation parameters (Table 2). Although the $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ values for both isomerizations are equal, the only difference is found in the $\Delta S^{\ddagger}$ values, indicating that the magnitude of $\Delta S^{\ddagger}$ controls the ratio of **7** and **8**. The attempted isomerization in CD_3CN, which was done in order to clarify the solvent effect, produced **1** and **2**.

Table 2. Activation Parameters of Isomerization between **7** and **8**

	$\Delta E^{\ddagger}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
7 to **8**	108	106	20.9
8 to **7**	108	106	8.8

Mechanism of the isomerization between **7** and **8** will be best explained as follows. Initially, the ring-opening of **7**, which is very slow at –18 °C, takes place at room temperature or above to form the carbocation **9**, while that of **8** gives the carbocation **10**. Both **9** and **10** would be stabilized by anchimeric assistance of the two benzene rings, which would serve as a driving force of the ring-opening. The carbocations **9** and **10** then undergo a conformational change to each other by free rotation about the carbon–carbon bond to give a mixture of **7** and **8**. The formation of the carbocation **11**, stabilized by the only one benzene ring, from **8** might be least possible. Thus, the formation of the episulfonium salt **12**, which might be produced from **11** by free rotation about the carbon–carbon bond followed by carbon–sulfur bond formation, was not detected during the isomerization of **7** and **8**. The larger $\Delta S^{\ddagger}$ value for the isomerization of **7** to **8** than that for the inverse process might indicate that the structural change of disorder in **7**, whose structure is more compact than that of **8**, is larger than that of **8** for the transition state that lead to the C–S bond cleavage.



In conclusion, for the first time, we have succeeded in the observation of the isomerization of episulfonium salts by using the isolated pure samples and in the detemination of the activation parameters for the isomerization.[10]

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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7 Dilution of the methylation mixture of **5** at –18 °C with Et_2O resulted in the separation of **7** in pure form as colorless crystals. The sulfonium salt **8** was isolated as colorless crystals in the same way.
8 **7**: mp >154 °C (dec); colorless crystals; ^{1}H NMR ($CDCl_3$, –20 °C) δ 1.52–1.64 (4H, m), 2.21–2.33 (2H, m), 2.44–2.57 (2H, m), 2.78 (3H, s), 3.50 (2H, d, J = 3.4 Hz), 3.90 (2H, d, J = 3.4 Hz), 6.81–6.88 (4H, m), 6.94–7.00 (4H, m); ^{13}C NMR (CD_3CN, –20 °C) δ 15.6, 26.3, 46.4, 48.5, 83.7, 121.5, 121.9, 127.8, 127.9, 140.1, 142.7. **8**: mp >152 °C (dec); colorless crystals; ^{1}H NMR ($CDCl_3$, –20 °C) δ 1.18–1.32 (4H, m), 1.65–1.77 (2H, m), 2.29–2.39 (1H, m), 2.49–2.57 (1H, m), 2.61 (3H, s), 3.53 (1H, br s), 3.63 (1H, d, J = 3.5 Hz), 4.02 (1H, br s), 4.22 (1H, d, J = 3.5 Hz), 7.22–7.28 (3H, m), 7.32–7.40 (4H, m), 7.48–7.53 (1H, m); ^{13}C NMR (CD_3CN, –20 °C) δ 17.2, 24.4, 25.9, 26.2, 26.3, 45.5, 46.3, 47.4, 48.9, 88.6, 89.0, 121.8, 121.9, 122.26, 122.29, 127.9, 128.1, 128.8, 128.9, 141.2, 143.2, 143.7, 143.8. Anal. Calcd for $C_{23}H_{23}BF_4S$: C, 66.04; H, 5.54%. Found: C, 65.97; H, 5.52% (performed on a mixture of **7** and **8**).
9 Attempted preparation of single crystals of **7** and **8** for X-ray crystallographic analysis was not successful.
10 Reactions of *cis*- and *trans*-2-butenes with ArSCl in the presence of $AgBF_4$ at –55 to 20 °C followed by addition of AcOH gave a 3:1 mixture of *erythro*- and *threo*-2-arylthio-3-acetoxybutenes; W. A. Smit, M. Z. Krimer, and E. V. Vorobeva, *Tetrahedron Lett.*, **1975**, 2451. See also E. A. Vorobieva, M. Z. Krimer, and W. A. Smit, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 2743.