Pergamon

Tetrahedron Letters 41 (2000) 8913–8916

TETRAHEDRON
LETTERS

Sulfuration of 9,9′-bibenzonorbornenylidenes by elemental sulfur: exclusive episulfide formation with retention of the configuration of alkenes

Yoshiaki Sugihara, Koichi Noda and Juzo Nakayama*

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570, Japan

Received 3 August 2000; revised 6 September 2000; accepted 14 September 2000

Abstract

Sulfuration of *syn*-bibenzonorbornenylidene (**5a**) by elemental sulfur in refluxing *o*-dichlorobenzene furnished the episulfide (**6a**) exclusively in 83% yield with retention of the configuration of **5a**, while that of *anti*-9,9′-bibenzonorbornenylidene (**5b**) under the same conditions resulted in the exclusive formation of the episulfide (**6c**) in 72% yield also with retention of the configuration of **5b**. Non-stereoselective sulfuration of **5a** and **5b** by S_2Cl_2 is also described. © 2000 Elsevier Science Ltd. All rights reserved.

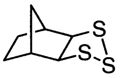
Keywords: sulfuration; 9,9′-bibenzonorbornenylidenes; episulfides; stereochemistry; retention of configuration.

Recent sulfuration studies of alkenes by elemental sulfur have reached the conclusion that the number of sulfur atoms, introduced into the double bond concerned, dramatically depends upon the structure of alkenes. Thus, the sulfuration of norbornene furnishes trithiolane (**1a**) and pentathiepane (**1b**) in the ratio 3.5:1.0,[1] while the sulfuration of dibenzobarrelene affords trithiolane (**2a**) and pentathiepane (**2b**) in the ratio 1.0:1.3.[2] On the other hand, the sulfuration of acenaphtho[1,2-*a*]acenaphthylene furnishes pentathiepane (**3**) exclusively,[3] whereas the sulfuration of highly congested 2,2′-biadamantylidene gives episulfide (**4**) exclusively.[2] However, these sulfuration studies do not provide any information about the stereochemistry of the reaction. Quite recently, we have synthesized *syn*-9,9′-bibenzonorbornenylidene (**5a**) and *anti*-9,9′-bibenzonorbornenylidene (**5b**),[4] which allow a stereochemical study of the sulfuration. We report here that sulfuration of these alkenes by elemental sulfur results in the exclusive formation of the corresponding episulfides with retention of the original stereochemistry.[5] Sulfurations of **5a** and **5b** with S_2Cl_2, which were carried out for comparison with that with elemental sulfur and proceeded in a non-stereoselective manner, are also described.

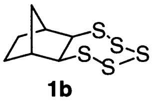
---

* Corresponding author. Fax: +81 48 858 3700; e-mail: nakaj@post.saitama-u.ac.jp

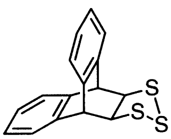
PII: S0040-4039(00)01605-1



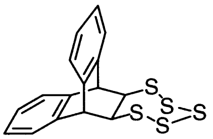
1a



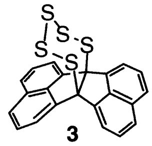
1b



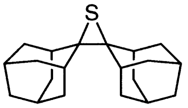
2a



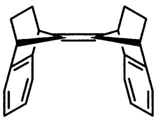
2b



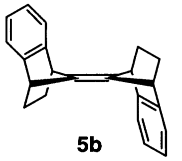
3



4



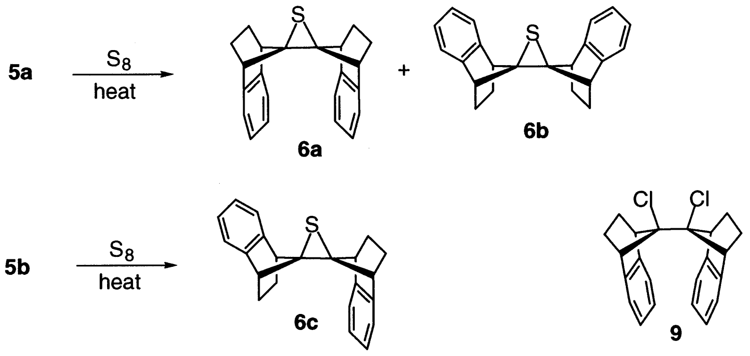
5a



5b

Results of sulfurations of **5a** and **5b** by elemental sulfur and S_2Cl_2 are summarized in Table 1.

Table 1
Sulfurations of **5a** and **5b** by S_8 and S_2Cl_2

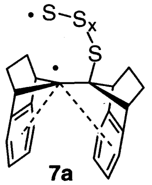


Entries	Alkenes	Reagents	Conditions	Products (yield, %)					
				Episulfides					
				6a	**6b**	**6c**	**9**	**5a**	**5b**
1	**5a**	S_8	o-$Cl_2C_6H_4$, reflux, 24 h	83[b]				16[b]	
2	**5a**	S_8	DMF, 135°C, 19 h	65[a]	14[a]			21[a]	
3	**5b**	S_8	o-$Cl_2C_6H_4$, reflux, 9 h			72[a]			12[a]
4	**5b**	S_8	DMF, 135°C, 10 h			89[a]			11[a]
5	**5b**	S_8	Neat, 18°C, 1.5 h[c]			100[b]			
6	**5a**	S_2Cl_2	CH_2Cl_2, rt, 6 h	34[a]		16[a]	7[a]		
7	**5b**	S_2Cl_2	CH_2Cl_2, −78°C, 2 h	11[a]		50[a]	26[a]		

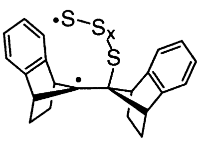
[a] Isolated yield.
[b] Yields determined by ^1H NMR.
[c] Carried out in a sealed tube.

Sulfuration of **5a** by elemental sulfur (1 equiv. as S_8) in refluxing *o*-dichlorobenzene for 24 h provided the episulfide (**6a**) as the sole product in 83% yield with recovery of **5a** in 16% yield (entry 1), whereas that in DMF at 135°C for 19 h gave two *syn*-episulfides (**6a**) and (**6b**)[4] in 65 and 14% yields, respectively, with recovery of **5a** in 21% yield (entry 2). On the other hand, the sulfuration of **5b** in refluxing *o*-dichlorobenzene for 9 h afforded *anti*-episulfide (**6c**) in 72% yield with recovery of **5b** in 12% yield (entry 3) and that in DMF at 135°C for 10 h gave **6c** in 89% yield with recovery of **5b** in 11% yield (entry 4). Heating **5b** and elemental sulfur neat afforded **6c** quantitatively (entry 5). Structures of episulfides **6a**–**c** were determined by comparison with the authentic samples.[4] These results show that *the sulfurations took place with complete retention of the original structure of **5a** and **5b***. The formation of the corresponding trithiolane and pentathiepane was not observed in any of the cases, even in trace amounts. This is probably due to the fact that the increasing number of sulfur atoms results in marked increase of steric repulsion between substituents.

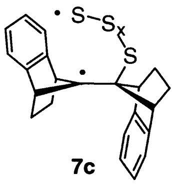
Two mechanisms can accommodate the observed stereochemistry of the sulfuration. One of them involves sulfuration by diradical $^{\bullet}S{-}S_x{-}S^{\bullet}$, which was generated by thermal processes involving homolytic cleavage of the cyclooctasulfur S_8.[6] For the sulfuration of **5a** in *o*-dichlorobenzene, the diradical adds the double bond from the ethylene chain side, but not the benzene ring side, to form another diradical intermediate (**7a**) exclusively, whereas this selectivity is weakened in a polar solvent DMF, and thus diradicals both (**7a**) and (**7b**) (adduct from the benzene ring side) are formed. Stabilization of the diradical **7a** by neighboring group participation of the two benzene rings would explain this selectivity.[7] Finally, the ring closure of **7a**, which is faster than the internal rotation about the C–C bond, takes place to afford **6a** with extrusion of $S_{(x+1)}$, while the same process of **7b** affords **6b** as the minor product in the sulfuration in DMF. On the other hand, the sulfuration of **5b** is free of such selectivity and affords the sole diradical (**7c**) to provide the episulfide **6c** as the final product. The other mechanism, though less probable, is a concerted one; cyclooctasulfur or its more reactive allotropes,[8] such as cyclohexasulfur S_6 (formed from the former thermally), may react with **5a** and **5b** through a transition state such as **8** to give episulfides in a concerted manner.



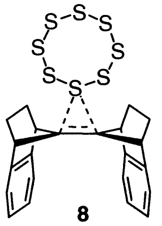
7a



7b

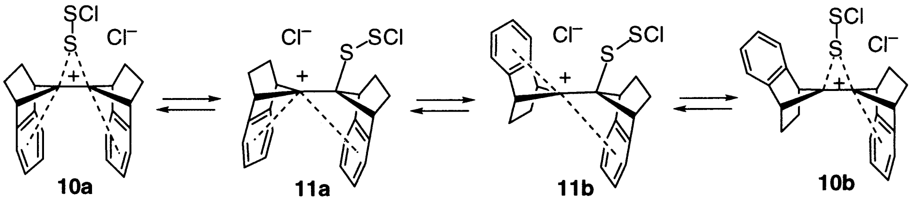


7c



8

Next, ionic sulfurations of **5a** and **5b** by S_2Cl_2 were carried out for comparison with those by elemental sulfur.[9] Sulfuration of **5a** by S_2Cl_2 (1 equiv.) in CH_2Cl_2 afforded **6a**, **6c** and *vic*-dichloride (**9**) in 34, 16 and 7% yields, respectively (entry 6).[10] Meanwhile, the sulfuration of **5b**, which proceeded even at −78°C, furnished **6a**, **6c** and **9** in 11, 50 and 26% yields, respectively (entry 7). The following may explain the results of sulfurations by S_2Cl_2. The initial adducts of **5a** and **5b** with S_2Cl_2, episulfonium salts (**10a**) and (**10b**),[11] would be in equilibrium with the ring-opened carbocation forms (**11a**) and (**11b**), which would be long-lived, compared to diradical species **7a**–**c**, because of the more effective neighboring group participation described in the preceding paper,[10] and hence are interconvertible to each other through internal rotation about the C–C bond. The elimination of SCl_2 from **11a** (**10a**) and **11b** (**10b**) affords **6a** and **6c**, respectively. However, we cannot rule out a possibility that the observed non-stereoselective episulfidation may partly result from the S_2Cl_2-catalyzed isomerization of **6a** and **6c**; separate experiments showed that **6a** and **6c** isomerize to each other by treatment with S_2Cl_2.[12] The observation of the S_2Cl_2-catalyzed isomerization indicates that the elimination of SCl_2 from **11a** and **11b** is probably reversible. The dichloride **9** is the adduct of **5a** and **5b** with molecular chlorine that exists in a small amount as the result of an equilibrium of SCl_2 (formed during the reaction) with S_2Cl_2.[13]



Acknowledgements

We appreciate financial support by the Sumitomo Foundation (to Y.S.) and Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References

1. Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* **1987**, *52*, 4937–4943.
2. Nakayama, J.; Ito, Y.; Mizumura, A. *Sulfur Lett.* **1992**, *14*, 247–250.
3. (a) Sugihara, Y.; Takeda, H.; Nakayama, J. *Tetrahedron Lett.* **1998**, *39*, 2605–2608. (b) Sugihara, Y.; Takeda, H.; Nakayama, J. *Eur. J. Org. Chem.* **1999**, 597–605.
4. Sugihara, Y.; Noda, K.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **2000**, *73*, in press.
5. (a) Sidhu, K. S.; Lown, E. M.; Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 254–263. (b) Nau, W. M.; Bucher, G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 1961–1970.
6. Oae, S.; Sato, R. In *Yuki Iou Kagaku (Gousei Hannou Hen)*; Oae, S., Ed.; Kagakudojin: Kyoto, 1982; Chapter 1.6.1.
7. (a) Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 6509–6510. (b) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, *J. Am. Chem. Soc.* **1978**, *100*, 6510–6512. (c) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. C.; Beno, M. M. A.; Christoph, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 7106–7121.
8. (a) Bartlett, P. D.; Lohaus, G.; Weis, C. D. *J. Am. Chem. Soc.* **1958**, *80*, 5064–5069. (b) Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971–4972.
9. Sulfuration of **5b** by Ph$_3$CSCl (1 equiv.), an episulfidation reagent of alkenes, in CH$_2$Cl$_2$ at room temperature afforded **6c** in 28% yield with recovery of **5b** in 72% yield, whereas **5a** was inert to Ph$_3$CSCl under the same conditions. For episulfidation with Ph$_3$CSCl, see: Abu-Yousef, I. A.; Harpp, D. N. *J. Org. Chem.* **1998**, *63*, 8654–8660.
10. Sugihara, Y.; Noda, K.; Nakayama, J. *Tetrahedron Lett.* **2000**, *41*, 8907–8911.
11. (a) Lautenschlager, F.; Schwartz, N. V. *J. Org. Chem.* **1969**, *34*, 3991–3998. (b) Tolstikov, G. A.; Lerman, B. M.; Umanskaya, L. I.; Struchkov, Y. T.; Espenbetov, A. A.; Yanovsky, A. L. *Tetrahedron Lett.* **1980**, *21*, 4189–4192.
12. Treatment of **6a** with S$_2$Cl$_2$ at room temperature for 4 h gave a mixture of **6a** (22%), **6c** (69%), and **10** (9%), while treatment of **6c** under the same conditions gave a mixture of **6a** (2%) and **6c** (98%).
13. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley: New York, 1988; p. 513.