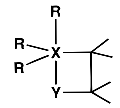
Experimental and Theoretical Evidence for Oxirane Formation Reaction of Pentacoordinate 1,2λ^6-Oxathietanes with Retention of Configuration

Takayuki Kawashima,* Fumihiko Ohno, Renji Okazaki,*
Hirotaka Ikeda,[†] and Satoshi Inagaki*,[†]

Department of Chemistry, Graduate School of Science
The University of Tokyo, 7-3-1 Hongo
Bunkyo-ku, Tokyo 113, Japan
Department of Chemistry, Faculty of Engineering
Gifu University, 1-1 Yanagido, Gifu 501-11, Japan

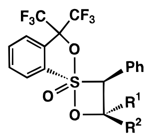
Received August 26, 1996

From our interest in diheteracyclobutanes **1** bearing highly coordinate main group elements at the neighboring position,[1,2] we have reported the synthesis and thermolysis of the pentacoordinate 1,2λ^6-oxathietane **2**.[3,4] Almost quantitative oxirane formation from **2** has suggested a possibility that the oxathietane is an intermediate of the Corey−Chaykovsky reaction of oxosulfonium ylides with carbonyl compounds.[3]

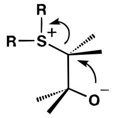


1

X=P, Si$^-$, Ge$^-$, Sn$^-$, S, Se
Y=O, NPh



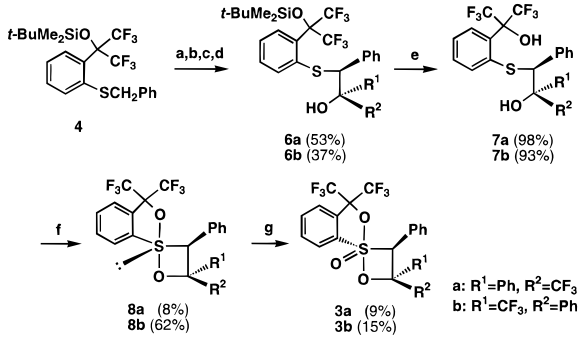
2: R^1=R^2=CF_3
3a: R^1=Ph, R^2=CF_3
3b: R^1=CF_3, R^2=Ph



anti-betaine

It has been proposed that the Corey−Chaykovsky reaction[5] involves the formation of an anti-betaine followed by a back side attack of an oxido anion on the β-carbon.[6] But, if the oxathietane is a real intermediate of the Corey−Chaykovsky reaction,[7] S−O bond heterolysis followed by C−C bond rotation is necessary for such an oxirane formation. Electrostatic interaction between the oxido anion and the sulfonium cation, which seems a driving force of the formation of the oxathietane ring, would resist the C−C bond rotation. In this case, an alternative mechanism such as a concerted mechanism or a front attack of the oxido anion without the C−C bond rotation can be expected to be operative. In order to elucidate these possibilities, we have decided to examine the stereochemistry of the oxirane formation. In this paper we wish to report the first example of the oxirane formation with retention of configuration and the theoretical study of this process.

Scheme 1[a]



[a] (a) 1.2 equiv of LDA, THF, −78 °C, 15 min; (b) $PhCOCF_3$ (**5**) THF, −78 °C, 15 min; (c) aqueous NH_4Cl; (d) FCC (SiO_2); (e) 2 equiv of *n*-Bu_4NF, THF, 0 °C, 30 min; (f) 1.0 equiv of Br_2, 2.0 equiv of Et_3N, CCl_4, 0 °C; 25 °C, 7 h; (g) *m*CPBA, Na_2HPO_4, CH_2Cl_2, 0 °C → 25 °C, 12 h.

Two diastereomers of pentacoordinate 1,2λ^6-oxathietanes **3a** and **3b** with the Martin ligand[8] were synthesized by the same method as previously reported (Scheme 1).[3] The separation of diastereomers **6a** and **6b** was nicely performed by flash column chromatography (FCC, SiO_2). The stereochemistry of **8a** and **8b** was determined by differential NOE experiments as follows: NOE between a methine proton of carbon-3 and ortho-protons of the phenyl group of carbon-4 was observed for (3*S*,4*R*)- or (3*R*,4*S*)-**8a** and not for (3*S*,4*S*)- or (3*R*,4*R*)-**8b**. Since the stereochemistry around a pentacoordinate sulfur and the relationship between the S=O group and the phenyl group at carbon-3 for **3** are considered to be the same as those reported for **2** and, furthermore, the relative stereochemistry around carbon-3 and carbon-4 is retained during the oxidation of **8**, **3a** and **3b** are concluded to have the structures as shown in Scheme 1.

Thermolysis of **3a** gave the corresponding oxirane **9a** along with **5**, phenyl-migrated ketone **10**, benzaldehyde (**11**), cyclic sulfinate **12**, a diastereomeric mixture of cyclic thioacetal *S*-oxides **13**, and cyclic thioacetal **14** (Scheme 2).[9] In sharp contrast to the thermolysis of **2**,[3] the yield of oxirane **9a** was

---

[†] Gifu University.

[1] Kawashima, T.; Okazaki, R. *Synlett* **1996**, 600−608. For pentacoordinate 1,2-oxaphosphetanes, see: Kawashima, T.; Kato, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 869−870. Kawashima, T.; Takami, H.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 4509−4510. For oxetanes having pentacoordinate group 14 elements, see: Kawashima, T.; Iwama, N.; Okazaki, R. *Ibid.* **1992**, *114*, 7598−7599. Kawashima, T.; Nishiwaki, Y.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 143−146. Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc*. **1993**, *115*, 2507−2508. For pentacoordinate 1,2-azaphosphetidines, see: Kawashima, T.; Soda, T.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1096−1098.

[2] For tetracoordinate 1,2-oxachalcogenetanes, see: (a) Kawashima, T.; Ohno, F.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 10434−10435. (b) Kawashima, T.; Ohno, F.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2094−2095.

[3] Ohno, F.; Kawashima, T.; Okazaki, R. *J. Am. Chem. Soc.* **1996**, *118*, 697−698.

[4] This compound can be classified to sulfurane oxides. For previous examples, see: Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 3155−3168. Perozzi, E. F.; Martin, J. C.; Paul, I. C. *Ibid.* **1974**, *96*, 6735−6744. Adzima, L. J.; Martin, J. C. *Ibid.* **1977**, *99*, 1657−1659. Lau, P. H. W.; Martin, J. C. *Ibid.* **1977**, *99*, 5490−5491. Rongione, J. C.; Martin, J. C. *Ibid.* **1990**, *112*, 1637−1638.

[5] For the Corey−Chaykovsky reactions, see: (a) Johnson, A. W.; LaCount, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 417−423. (b) Corey, E. J.; Chaykovsky, M. *Ibid.* **1962**, *84*, 3782−3783. (c) Corey, E. J.; Chaykovsky, M. *Ibid.* **1965**, *87*, 1353−1364. (d) Aubé, J. In *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Synthetic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 1, pp 822−825. For the synthesis of optically active oxiranes via sulfur ylides, see: (e) Furukawa, N.; Sugihara, Y.; Fujihara, H. *J. Org. Chem.* **1989**, *54*, 4222−4224. (f) Breau, L.; Ogilvie, W. W.; Durst, T. *Tetrahedron Lett.* **1990**, *31*, 35−38. (g) Solladié-Cavallo, A.; Adib, A. *Tetrahedron* **1992**, *48*, 2453−2464. (h) Aggarwal, V. K.; Abdel-Rahman, H.; Jones, R. V. H.; Lee, H. Y.; Reid, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 5973−5974. (i) Aggarwal, V. K.; Thompson, A.; Jones, R. V. H.; Standen, M. *Tetrahedron: Asymmetry* **1995**, *6*, 2557−2564. (j) Li, A.-H.; Dai, L.-X.; Hou, X.-L.; Huang, Y.-Z.; Li, F.-W. *J. Org. Chem.* **1996**, *61*, 489−493. For the related reactions of aminosulfoxonium ylides, see: (k) Johnson, C. R. *Acc. Chem. Res.* **1973**, *6*, 341−347.

[6] Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc.* **1971**, *93*, 5303−5305. Durst, T.; Viau, R.; Van Den Elzen, R.; Nguyen, C. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1334−1336. Townsend, J. M.; Sharpless, K. B. *Tetrahedron Lett.* **1972**, 3313−3316. Durst, T.; Johnson, C. R.; Schroeck, C. W.; Shanklin, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 7424−7431.

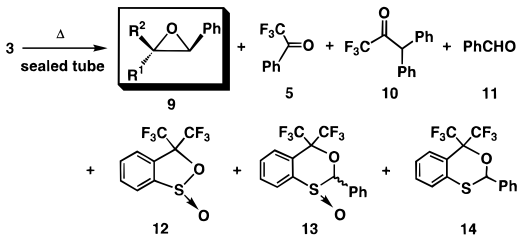
[7] In the formation reaction of spiropentanes by the reaction of sulfonium cyclopropylides with carbonyl compounds, a mechanism involving an oxathietane was proposed as an alternative one involving a ring expansion to a σ-sulfurane having an oxirane ring followed by reductive elimination of the sulfide, see: Bogdanowicz, M. J.; Trost, B. M. *Tetrahedron Lett.* **1970**, 887−890. Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5298−5307.

[8] For the bidentate ligand which is very effective in stabilizing the higher coordination states of nonmetallic elements, see: Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049−1053.

[9] Products **5**, **10**, **12**, and **13** are thought to be formed via a mechanism similar to that reported in ref 2b. Benzaldehyde (**11**) and **14** seem to be formed as follows: the oxosulfonium ylide, which is formed by retroaddition of **3** together with **5**, reacts with **13** to give **14** and the corresponding inner oxosulfonium oxide, which undergoes C−S bond cleavage to afford **11** and **12**.

S0002-7863(96)02997-6 CCC: $12.00 © 1996 American Chemical Society

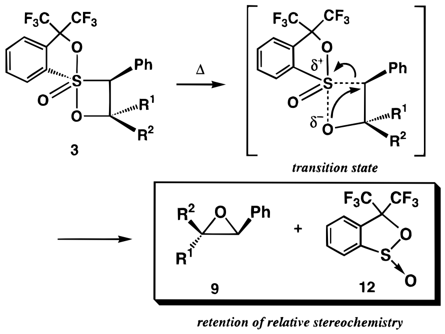
Scheme 2



3	R^1	R^2	conditions	Products (yield[a)]/%)						
				9	5	10	11	12	13	14
a	**Ph**	**CF_3**	120 °C, 3.5 h[b)]	12	61	20	4	41	50 (30:20)[d)]	9
a	**Ph**	**CF_3**	110 °C, 13 h[c)]	30	49	12	-[e)]	53	36 (17:19)	10
b	**CF_3**	**Ph**	120 °C, 12.5 h[b)]	9	72	12	5	33	60 (35:25)	7
b	**CF_3**	**Ph**	130 °C, 12 h[c)]	28	33	35	-[e)]	71	25 (12:13)	4

[a] Obtained by ^{1}H and ^{19}F NMR. [b] In $CDCl_3$. [c] In THF−C_6D_6 (6:1). [d] The ratio of two diastereomers was shown in the parentheses. [e] Observed by GC-MS.

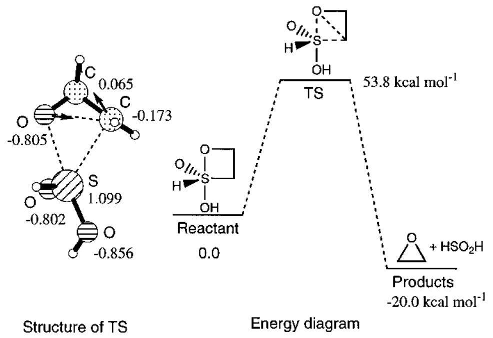
Scheme 3



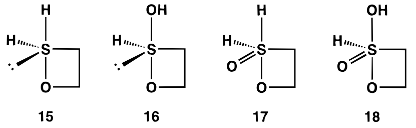
quite low, but only a single isomer was obtained. Similarly, the thermolysis of **3b** afforded the other isomer **9b** stereospecifically.

Differential NOE experiments showed that **9a** and **9b** are (*Z*)- and (*E*)-isomers, respectively, indicating that the oxirane formation proceeds with retention of configuration (Scheme 3). That is, the stereochemistry of the oxirane formation was completely reverse to that expected for the back side attack of the oxido anion. Pentacoordinate 1,2λ^6-oxathietanes **3** are formally considered as [2 + 2]cycloadducts of oxosulfonium ylides with carbonyl compounds. Furthermore, the 1,2-oxathietane formation was shown to be a no activation energy process by the previous theoretical calculation.[10] Our study on the isomerization of tetracoordinate (*E*)- and (*Z*)-1,2λ^4-oxathietanes via retroaddition−recombination of sulfur ylides with benzophenone also suggests the possibility that the 1,2-oxathietanes are intermediates of the Corey−Chaykovsky reaction.[2b] These results strongly suggest that 1,2-oxathietanes are intermediates of the reaction of the sulfur ylides with carbonyl compounds and decompose to give the oxirane with retention of configuration. The Corey−Chaykovsky reaction has usually been carried out in the presence of salts which were formed in the preparation of sulfur ylides. So, we investigated the effect of salts on the stereochemistry of oxirane formation. Both thermolyses of **3a** and **3b** in the presence of 5 equiv of lithium bromide in THF−C_6D_6 (6:1) gave a mixture of oxiranes **9a** and **9b** in the ratios of 17:7 and 2:16, respectively, in sharp contrast to the results in the absence of the salts (Scheme 2), indicating that lithium salts can assist the back side attack. This probably explains why the stereochemistry of the typical Corey−Chaykovsky reaction is completely different from that of the present oxirane formation. Therefore, the present reaction can be recognized as a salt-free Corey−Chaykovsky reaction.[11]

Scheme 4



The present unprecedented results prompted us to study theoretically the oxirane formation from 1,2-oxathietanes. Transition states for the concerted oxirane formation from simple 1,2-oxathietanes **15**−**18** as model compounds were located by ab initio calculations (RHF/4-31G*).[12] The activation energies



for the process were calculated to be 28.2, 46.7, 45.3, and 53.8 kcal mol^{-1} for **15**, **16**, **17**,[13] and **18**, respectively. The structure of the transition state and energy diagram for the oxirane formation from **18** are shown in Scheme 4. The values of activation energy correspond to how much the substituents can stabilize the positively polarized central sulfur atom; oxo and hydroxyl groups destabilize the positive charge on the sulfur atom more than hydrogen. A similar polarized transition state was reported for the apical−equatorial ligand coupling of sulfuranes.[14] This is the first finding for oxirane formation pathway from 1,2-oxathietanes, which can be recognized as a carbon−oxygen ligand-coupling reaction of sulfuranes.[15]

In conclusion, we have demonstrated the first example for the oxirane formation with retention of configuration, which can be regarded as a salt-free Corey−Chaykovsky reaction. A theoretical study revealed that the oxirane formation proceeds via a concerted mechanism involving a polarized transition state.

Acknowledgment. This work was partially supported by Kurata Research Grant (T.K.) and Grant-in-Aid for General Scientific Research (B) No. 07454160 (T.K.) from the Ministry of Education, Science and Culture. F.O. thanks Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. We thank Sin-etsu Chemical, Central Glass, and Tosoh Akzo Co., Ltd., for gifts of silyl chlorides, hexafluorocumyl alcohol, and alkyllithiums, respectively.

Supporting Information Available: An experimental procedure for the synthesis of **3a** and **3b** and physical and spectral data for **3a**, **3b**, **6**−**8**, **10**, and **13** (8 pages). See any current masthead page for ordering and Internet access instructions.

JA9629975

---

(10) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1987**, *109*, 1−14.

(11) The first example was reported in ref 5a, but the reaction was considered to proceed via a betaine.

(12) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92, Revision C; Gaussian, Inc.: Pittsburgh, PA, 1992.

(13) Another transition state from the S═O apical pseudorotamer was located for **17** (30.7 kcal mol^{-1}).

(14) Moc, J.; Dorigo, A. E.; Morokuma, K. *Chem. Phys. Lett.* **1993**, *204*, 65−72 and references cited therein.

(15) The ligand-coupling reactions involving a sulfurane intermediate have been reported. For a recent review, see: Oae, S.; Uchida, Y. *Acc. Chem. Res.* **1991**, *24*, 202−208. For a recent example of the ligand coupling reaction from sulfuranes which was spectroscopically identified, see: Ogawa, S.; Sato, S.; Furukawa, N. *Tetrahedron Lett.* **1992**, *33*, 7925−7928.