Structure and Natural Bond Orbital Analysis of Oxiranes Substituted with a Group 14 Element. A Comment of SN2 Regioselectivity

Taketo Ikeno, Jun Harada, and Shuji Tomoda*
Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902

(Received January 27, 1999; CL-990055)

Crystal structure analysis of oxiranes substituted with a group 14 element revealed that silyl and stannyl groups lengthened their α C-O bonds. Natural bond orbital analysis showed that silyl group raised the energy level of α C-O σ orbital and lowered that of α C-O σ* orbital. It was suggested that the former might lengthen the α C-O bond and that the latter should affect the regioselectivity in ring-opening reactions.

Oxiranes react with a variety of nucleophiles to give ring-opened products. The ring carbons of substituted oxiranes are different in steric and electronic environment. In alkyl-substituted oxiranes, less hindered carbons are preferentially attacked by nucleophiles for steric reasons.[1] In the case of α,β-epoxysilanes and α,β-epoxystannanes, however, the carbons proximate to the silicon or the tin substituent are selectively attacked[2,3] even if the substituents have large steric hindrance. A number of explanations have been proposed for the effect of silyl group, but few accounts in terms of structure of oxiranes have been reported.[3-6] In this communication, we report X-ray crystal structure analysis and natural bond orbital (NBO) analysis of oxiranes substituted with a group 14 element, and discuss the relation between their structures and the regioselectivity in ring-opening reactions.

In order to compare the C-O bond lengths of oxiranes systematically, we synthesized triphenylmethyloxirane (**1**),[7] triphenylsilyloxirane (**2**), and triphenylstannyloxirane (**3**), and

1: M = C
2: M = Si
3: M = Sn

determined their molecular structures (Figure 1).[8] The C-O bond lengths of the oxiranes determined by X-ray analysis are shown in the upper part of Table 1. The α C-O bond of oxirane **1** (1.437 Å) is slightly shorter than the β C-O bond (1.446 Å). On the contrary, the α C-O bond of silyloxirane **2** (1.456 Å) is longer than the β C-O bond (1.435 Å) by 0.02 Å. The α C-O bond of stannyloxirane **3** (1.468 Å) is also longer than the β C-O bonds (1.441 Å) by 0.03 Å. Furthermore, though the bond lengths of the β C-O bonds of **2** and **3** are almost the same as that of the C-O bonds of **1**, the α C-O bonds of **2** and **3** are longer than the C-O bonds of **1**. These results clearly show that silyl and stannyl groups lengthen their α C-O bonds.

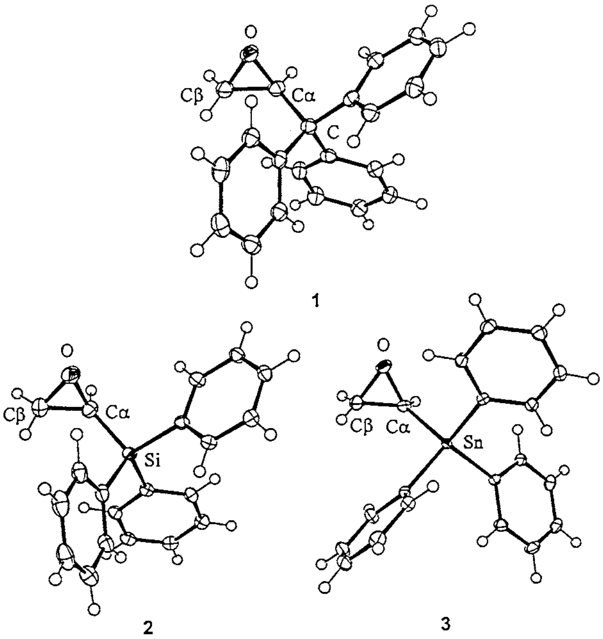


Figure 1. The ORTEP drawings of oxiranes **1**, **2**, and **3**.

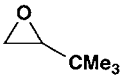
Table 1. C-O bond lengths (Å) of oxiranes substituted with a group 14 element obtained by X-ray structure analysis[a] and calculation[b]

		Group 14		
	Bond	C	Si	Sn
Exp.[a]	α C-O	1.437(2)	1.456(3)	1.468(3)
	β C-O	1.446(2)	1.435(3)	1.441(3)
Calc.[b]	α C-O	1.435	1.460	
	β C-O	1.436	1.422	

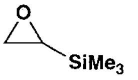
[a] X-ray structure of oxiranes **1**, **2**, and **3**. [b] Calculated strucutre of oxiranes **4** and **5** optimized at B3LYP/6-31G(d).

To investigate the reason for this bond elongation and the relation between the elongation and regioselectivity in ring opening reactions, electronic structure calculation was carried out.[9] *t*-Butyloxirane (**4**) and trimethylsilyloxirane (**5**) were selected as model compounds because of their simple structures. The structures were optimized at the B3LYP/6-31G(d) level. As shown in the lower part of Table 1, the calculated structures coincided well with the experimental results. The distance of the α C-O bond of **4** is almost the same as that of the β C-O bond. On the contrary, the α C-O bond of **5** is longer than the β C-O bond. Furthermore the α C-O bond of **5** is the longest among the C-O bonds of **4** and **5**. In particular, the agreement between the theoretical and experimental bond lengths demonstrates the validity of the optimized structures at the B3LYP/6-31G(d) level.

NBO analysis[10] was next examined at HF/6-31G(d) using



4



5

Table 2. Orbital energies and electron densities of α and β C-O bonds of epoxides **4** and **5**[a]

	Energy Level/ a.u.		Electron Density	
Orbital	**4**	**5**	**4**	**5**
σ (α C-O)	-0.90001	-0.84957	1.97683	1.97512
σ (β C-O)	-0.87714	-0.90301	1.97860	1.98150
σ^* (α C-O)	0.51603	0.47701	0.02825	0.02623
σ^* (β C-O)	0.50533	0.52596	0.02161	0.01999

[a] Calculation was performed at HF/6-31G(d) // B3LYP/6-31G(d).

the structures optimized as above. The energy levels and the electron density of bonding (σ) and antibonding (σ^*) orbitals of the α and the β C-O bonds of **4** and **5** were obtained (Table 2). First of all, α regioselectivity in nucleophilic ring-opening reactions of silyloxiranes can be explained in terms of the energy level of σ^* orbitals. It is generally accepted that the bond that has lower σ^* orbital is more sensitive to nucleophilic attack in S_N2 reaction. The energy level of α C-O σ^* orbital is higher than that of β C-O σ^* orbital in **4**. On the contrary, that of α C-O σ^* orbital is lower than that of β C-O σ^* orbital in **5**. This result coincided with known experimental data, that is, β regioselectivity of **4**[1] and α regioselectivity of **5** in ring-opening reactions.[3] Furthermore, the energy level of α C-O σ^* orbital of **5** is the lowest among all the C-O σ^* orbitals. Actually, we measured the pseudo first-order reaction rates of **4** and **5** with 10 molar amounts of tetrabutylammonium bromide in THF-H_2O (1:1) at 25° C, respectively.[11] The reaction rate of **5** was 44 times as large as that of **4**. From these results, it is strongly suggested that silyl groups lower the energy level of their α C-O σ^* orbitals, which enhances the reactivity of their α C-O bonds.

In agreement with the above conclusions, the changes in C-O bond lengths can be explained in terms of electron density. It is considered that within compounds of similar structures, the less electron density a σ orbital accommodates and the more electron density a σ^* orbital carries, the longer the σ bond. As shown in Table 2, the electron density in β C-O σ orbital of **4** is smaller than that of **5** and the electron density in β C-O σ^* orbital of **4** is larger than that of **5**. This indicates that the β C-O bond of **4** is longer than that of **5**, which is proved by X-ray structure. That is, the β C-O bond of **1** is longer than that of **2**. On the other hand, the electron density in α C-O σ^* orbital of **4** is larger than that of **5**, but the electron density in α C-O σ orbital of **5** is smaller than that of **4**. Although the electron density in σ and σ^* orbital of **4** and **5** gives an opposite influence on the relative bond lengths, the observation from the X-ray structure that the α C-O bond of **2** is longer than that of **1** reveals that reduced electron density in α C-O σ orbital of **5** plays a dominant role on the bond length. Decrease in the electron density in α C-O σ orbital of **5** is derived from the rise of its energy level. From Table 2, the energy level of α C-O σ orbital of **5** is much higher than that of **4**. It is known that in electron delocalization interaction, the smaller the energy difference between interactive orbitals is, the larger the electron delocalization occurs.[12] Hence, the rise of the energy level of α C-O σ orbital of **5** enhances the electron delocalization interaction between the σ orbital and the nearby unoccupied orbitals.

In conclusion, first systematic comparison of X-ray structures of oxiranes substituted with a group 14 element has revealed that silyl and stannyl groups lengthen their α C-O bonds. A correlation is observed between the bond length and the regioselelctivity in epoxide ring-opening. Silyl group weakens α C-O bond leading to the rise of the occupied σ orbital energy level and reduction in the energy level of α C-O σ^* orbital, which ultimately affects the S_N2 regioselectivity.

References and Notes

1 R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

2 J. M. Chong and E. K. Mar, *J. Org. Chem.*, **57**, 46 (1992).

3 For review, see P. F. Hudrlik and A. M. Hudrlik, in "Advances in Silicon Chemistry," ed by G. L. Larson, JAI Press, Greenwich, CT (1993), Vol. 2, p 1; E. Colvin, in "Silicon in Organic Synthesis", Butterworth, London (1981).

4 J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 2870 (1963).

5 J. J. Eisch and C. S. Chin, *J. Organomet. Chem.*, **358**, C1 (1988); P. F. Hudrlik, D. Ma, R. S. Bhamidipati, and A. M. Hudrlik, *J. Org. Chem.*, **61**, 8655 (1996); P. F. Hudrlik, L. Tafesse, and A. M. Hudrlik, *J. Am. Chem. Soc.*, **119**, 11689 (1997).

6 Six X-ray structures of α,β-epoxysilanes have been reported, but systematic analysis of C-O bond lengths has not been done. U. Siriwardane, S. S. C. Chu, and J. D. Buynak, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **45**, 531 (1989); G. A. Molander and K. Mautner, *J. Org. Chem.*, **54**, 4042 (1989); K. Yamamoto, Y. Kawanami, and M. Miyazawa, *J. Chem. Soc., Chem. Commun.*, **1993**, 436; T. Kawai, M. Isobe, and S. C. Peters, *Aust. J. Chem.*, **48**, 115 (1995); M. M. Kabat, *J. Org. Chem.*, **60**, 1823 (1995). D. M. Hodgson, P. J. Comina, and M. G. B. Drew, *J. Chem. Soc., Perkin Trans I*, 1997, 2279.

7 Triphenylmethyloxirane (**3**) was prepared from triphenylvinylmethane by treatment with dimethyldioxirane in 82% yield.

8 Crystal data **1**: $C_{21}H_{18}O$, $MW = 286.35$, triclinic, P-1, $a = 9.7559(17)$, $b = 9.9377(9)$, $c = 8.8608(13)$ Å, $\alpha = 94.547(11)$, $\beta = 101.914(14)$, $\gamma = 113.377(9)°$, $V = 759.03(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.253$ gcm^{-3}, $T = 90$ K, $R1(wR2) = 0.043(0.108)$, number of unique reflections 2225. **2**: $C_{20}H_{18}OSi$, $MW = 302.43$, monoclinic, $C2/c$, $a = 16.710(2)$, $b = 10.7388(17)$, $c = 18.617(2)$ Å, $\beta = 104.765(9)°$, $V = 3230.5(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.244$ gcm^{-3}, $T = 90$ K, $R1(wR2) = 0.066$ (0.171), number of unique reflections 7101. **3**: $C_{20}H_{18}OSn$, $MW = 393.03$, triclinic, P-1, $a = 9.4537(19)$, $b = 11.1147(16)$, $c = 9.1100(13)$ Å, $\alpha = 98.988(14)$, $\beta = 113.421(12)$, $\gamma = 69.907(14)$ °, $V = 824.7(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.583$ gcm^{-3}, $T = 90$ K, $R1(wR2) = 0.025$ (0.057), number of unique reflections 7258.

9 All the calculations were performed using Gaussian 94. (Revision D.1): Gaussian, Inc., Pittsburgh PA, (1995).

10 A. E. Reed and F. Weinhold, *J. Chem. Phys.*, **78**, 4066 (1983); A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, **88**, 889 (1988).

11 Reaction rate was measured at pH 7 by titration with HBr solution according to the literature; P. L. Nichols Jr. and J. Ingham, *J. Am. Chem. Soc.*, **77**, 6547 (1955); W. L. Petty and P. L. Nichols Jr., *J. Am. Chem. Soc.*, **76**, 4385 (1954).

12 T. A. Albright, J. K. Burdett, and M.-H. Whangbo, "Orbital Interactions in Chemistry," Wiley, New York (1985); I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," Wiley, London (1976).