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Definition and design of diagonalization reactions. Reactions of 1,2-heteraazetidine *N*-oxides

Satoshi Inagaki,[a,*] Hirotaka Ikeda[a] and Takayuki Kawashima[b]

[a]*Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan*
[b]*Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

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Abstract

We have defined diagonalization reactions as a concerted bond formation between the diagonal saturated atoms in cyclic molecules and designed the reactions of 1,2-heteraazetidine *N*-oxides to produce heteracyclopropanes with the extrusion of HNO. Analysis of the bond interactions at the transition states suggested the reactivities of the diagonalization reactions are controlled by the strains of the incipient rings of the transition structures. © 1999 Elsevier Science Ltd. All rights reserved.

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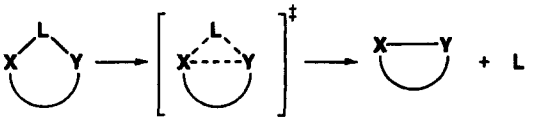
Definition of a new chemical reaction is meaningful to attract and concentrate attention on the design and understanding of the reaction. In the present work, we have defined the diagonalization reactions as a concerted bond formation between the diagonal atoms in cyclic saturated compounds **1** to produce the contracted ring molecules **2** by extruding a part Y of the original rings (Eq. 1) and designed the reactions of 1,2-heteraazetidine *N*-oxides **3–7** that give heteracyclopropanes and HNO (Eq. 2).



1 **2** (1)

* Corresponding author. Tel: +81-58-293-2611; fax: +81-58-230-1893; e-mail: inagaki@apchem.gifu-u.ac.jp

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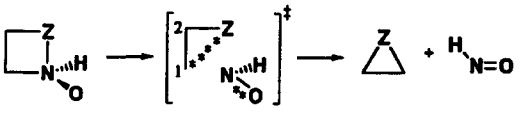


(2)

3, Z = CH_2
4, Z = NH
5, Z = O
6, Z = PH
7, Z = S

The diagonalization reaction of azetidine *N*-oxide (**3**) was shown by the intrinsic reaction coordinate calculations at the B3LYP/6-31G* level to proceed via a concerted pathway,[1,2] though its activation energy was fairly high (54.5 kcal/mol). We therefore attempted to design more reactive heteraazetidine *N*-oxides. We assumed that the activation energy would be controlled by the strain of the incipient three-membered ring at the transition state, and attempted to relax the strain by replacing the methylene group next to the nitrogen atom by a hetero atom. The strains of small ring molecules were previously shown to be relaxed by the increasing bonding property or the decreasing antibonding property of the delocalization of σ electrons between the geminal ring bonds (Fig. 1).[3] The relaxation was also previously suggested[3] to increase with the atomic number of the hetero atoms in the same row of the periodic table due to the lone-pair effect and as the row of the ring elements is higher. Therefore, the ring strains at the transition states were expected to decrease in the order of **3** (Z=CH_2)>**4** (Z=NH)>**5** (Z=O)>**6** (Z=PH)>**7** (Z=S). The reactivities should increase in the reverse order (**3**<**4**<**5**<**6**<**7**).

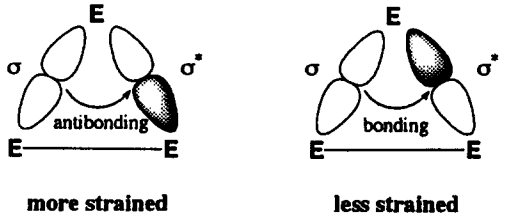


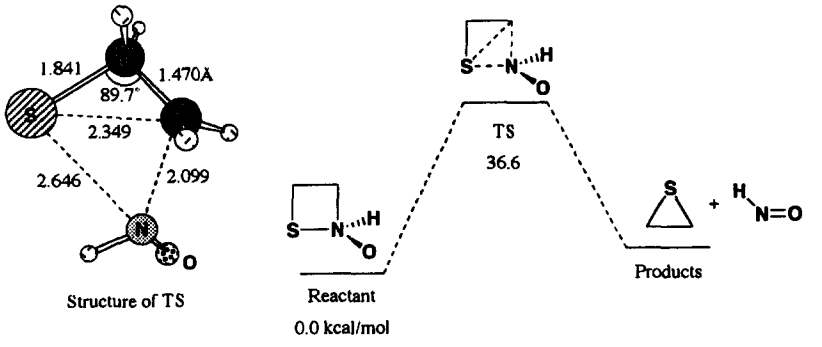
Figure 1. Geminal delocalization of σ-electrons and ring strains

The activation energies of **4**–**7** were calculated to be 47.2, 41.9, 38.1, 36.6 kcal/mol, respectively (Table 1).[1,4] The order of reactivities is in agreement with the prediction. The activation energy of the diagonalization reaction of **7** (Scheme 1) is significantly lower (about 18 kcal/mol) than that of **3**. The reaction could be observed experimentally.

Table 1
Activation energies of the diagonalization reactions of the heteraazetidine *N*-oxides

Compounds	Z	$\Delta E^{\ddagger a}$
3	CH_2	54.5
4	NH	47.2
5	O	41.9
6	PH	38.1
7	S	36.6

[a]Activation energies (kcal/mol) based on the most stable conformer of the reactants and transition states.



Scheme 1.

We investigated the bond interactions at the transition states by the method previously developed.[5,6] The calculated interbond energies (IBE)[7] confirmed the order of the predicted transition state strains (Fig. 2). The geminal delocalization is antibonding between the C1-Z and C2-Z bonds at the transition state of **3**. By contrast, the geminal delocalizations in **4**–**7** are bonding. The bonding property increases in the order of **4**<**5**<**6**<**7**. These results suggest that the ring strains at the transition states should control the reactivities of **3**–**7**.

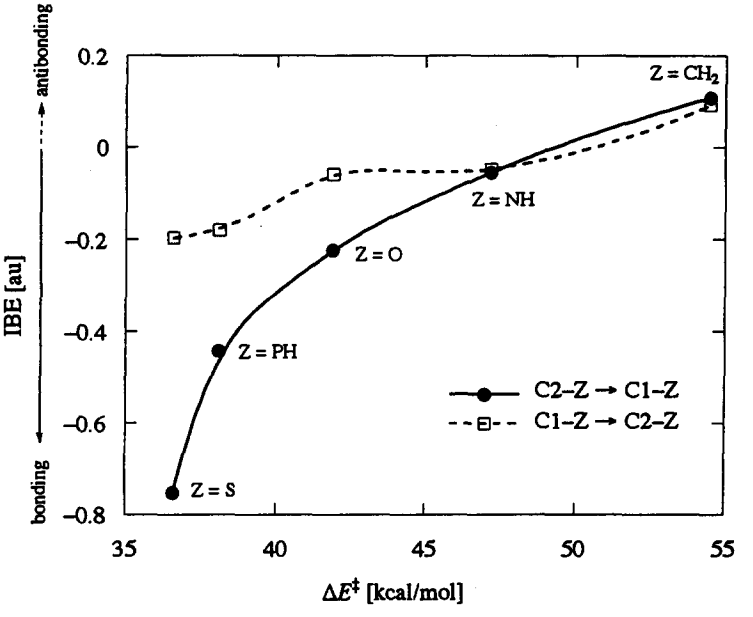


Figure 2. Activation energies vs interbond energies of geminal delocalization between the C1-Z and C2-Z bonds at the transition states in **3**–**7**

Thermolyses of 1,2λ^6-oxathietanes and 1,2λ^4-oxaselenetanes were previously reported to give oxiranes with retention of the configuration,[8] demonstrating that the reactions proceed in a concerted manner. These thermolyses are the first examples of the diagonalization reaction.

In summary, we have defined the diagonalization reaction and designed some reactions of 1,2-heteraazetidine *N*-oxides. The reactivities should be controlled by the ring strains at the transition states.

References

1. The geometry optimization was carried out by the density functional theory calculations at the B3LYP/6-31G* level using Gaussian 94 program.[2] All geometries examined here were checked by the frequency calculations. All transition structures were followed by the intrinsic reaction coordinate calculations toward the reactant and the product sides.
2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. A.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Reploge, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision C.3*; Gaussian: Pittsburgh, 1995.
3. The geminal delocalization is unexpectedly antibonding as usual since the hybrid orbitals on the central atom appreciably interact with each other, while the orbitals are orthogonal to each other. In contrast, the geminal delocalization is bonding where the interaction is weak. See: (a) Inagaki, S.; Goto, N.; Yoshikawa, K. *J. Am. Chem. Soc.* **1991**, *113*, 7144. (b) Inagaki, S.; Yoshikawa, K.; Hayano, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3706. (c) Inagaki, S.; Ishitani, Y.; Kakefu, T. *J. Am. Chem. Soc.* **1994**, *116*, 5954.
4. The reactant containing a silicon atom ($Z=SiH_2$) was not located as a stationary point. The geometry optimization of 1,2-azasiletidine *N*-oxide led to five-membered ring 1,2,5-oxazasilolidine.
5. (a) Inagaki, S.; Ikeda, H. *J. Org. Chem.* **1998**, *63*, 7820 and references cited therein. (b) Ikeda, H.; Naruse, Y.; Inagaki, S. *Chem. Lett.* **1999**, 363.
6. The 6-31G* basis set was used for the analysis of the bond interactions at the transition structures optimized by the density functional theory calculations.[1] The application of the bond model for transition states[5a] to the diagonalization reactions showed that the electronic structures of the transition states are close to the products. Therefore, we analyzed the bond interactions at the transition states which contain the three-membered rings.
7. Inagaki, S.; Yamamoto, T.; Ohashi, S. *Chem. Lett.* **1997**, 977. The interaction between the bond orbitals, i and j was estimated by the interbond energy (IBE) defined as below:

$$\mathrm{IBE}(i, j)=P_{ij}(F_{ij}+H_{ij})$$

where P_{ij}, F_{ij}, and H_{ij} are the elements of the density, Fock, and core Hamiltonian matrixes, respectively.
8. (a) Kawashima, T.; Ohno, F.; Okazaki, R.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 12455. (b) Ohno, F.; Kawashima, T.; Okazaki, R. *Chem. Commun.* **1997**, 1671.