Relative Stability for the Structural Isomers of Producing Fused-Ring Systems from Acyclic Substrates : *Ab Initio* Study

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Electrophilic substitution reactions of the molecules with an allylsilane group have been extensively applied to the organic synthesis.[1-10] In particular, the electrophilic reactions of acyclic polyolefins having the allylsilane have been applied to the synthesis of 6-, 7-, 8-, and 9-membered cyclic compounds. In the 6-, 7-, and 9-membered cyclic products, the methylenecycloalkanes with an exocyclic double bond are synthesized, while, in the 8-membered cyclic products, the 7-methoxy-1-methylcyclooctene with a double bond on the cyclic skeleton is synthesized.

In the experiments of van der Gen *et al.*,[1] the acyclic aldehyde having no allylsilane group under methanol conditions was completely cyclized to a cyclic olefin having a double bond. That is, the cyclization of 5-methyl-5-hexenal gives all three possible alkene isomers (endo- and exo-cyclic delocalized isomers) of 6-membered cyclic compound. Meanwhile, in the experiments of Fleming *et al.*,[2-4] the acyclic acetals with an allylsilane and vinylsilane groups cyclized to give the methylenecyclohexane and methylcyclohexene, respectively. Recently, by the experimental results of Kang *et al.*,[8-9] Lewis acid-induced intramolecular annulation of the allylsilanes with an electrophilic group was applied to a regioselective formation of several cyclic systems. The cyclizations of the acyclic alkenes with an allylsilane group give the methylenecyclohexane, methylenecycloheptane, methylcyclooctene, and methylenecyclononane, respectively. That is, in these cyclizations, the site of the double bond has been controlled by the number of the carbon atoms in acyclic skeleton.

By the above experimental results, in the 6-membered cyclic products, the methylenecyclohexane with an exocyclic double bond and the methylcyclohexene with a double bond on the cyclic skeleton are synthesized. While, in the 8-membered cyclic products, the methylcyclooctene with a double bond on the ring is easily synthesized. To analyze the experimental findings, we carried out systematic calculations for the 6-, 7-, and 8-membered cyclic compounds with the same accuracy. The geometrical structures of the cyclic compounds are fully optimized using *ab initio* Hartree-Fock (HF) and second-order Mϕller-Plesset (MP2) methods with the 6-311+G** basis set. After the optimization, the harmonic vibrational frequencies of those compounds are evaluated to confirm the existence of a stable structure at the HF/6-311+G** level. The Gaussian 94 program was used.[11] We represented the relative stabilities and structures of the cyclic compounds calculated with the MP2/6-311+G** level.

Three schematic potential energy diagrams and optimized structures for the structural isomers of the 6-, 7-, and 8-membered cyclic compounds are drawn in Figure 1. All optimized geometrical structures of the cyclic compounds are local minima without an imaginary frequency. The geometrical isomers of the 6-, 7-, and 8-membered cyclic compounds with higher potential energy are not represented. The structures of the cyclic compounds are classified to be chair and boat types except for 5-methoxy-1-methylcyclohexene with fused-ring form. In these compounds, the optimized structures of the chair types are more stable than those of the corresponding boat types, respectively. The cyclic structures of the methylcycloalkenes with a methyl group are more symmetric than those of the corresponding methylenecycloalkanes with a methylene group. A methoxy group is substituted as a horizontal or vertical direction on the cyclic skeleton. In the most stable structures of 6-, 7-, and 8-membered cyclic compounds, the geometrical conformation between three hydrogen atoms of a methoxy group and a carbon atom on the ring bonded to a oxygen atom is optimized as an eclipsed form. The structures of the 6- and 8-membered cyclic compounds are more symmetric than those of the 7-membered cyclic compounds.

As shown in Figure 1, the lowest potential energies of the 6-, 7-, and 8-membered cyclic compounds are set equal to zero, respectively. The chair types of these cyclic compounds are more stable than the boat types. In the 6- and 7-membered cyclic compounds, the methylenecyclohexanes with a methylene group are more stable than the methylcyclohexenes with a methyl group. That is, the structures with an exocyclic double bond are more stable than those with a double bond on the ring. While, in the 8-membered cyclic compound, the methylcyclohexenes with a methyl group are more stable than methylenecyclohexanes with a methylene group. In the 6- and 8-membered cyclic compounds, the structures substituted by a methoxy group as a horizontal direction are more stable than those substituted by a methoxy group as a vertical direction. While, in the 7-membered cyclic compounds, the structures substituted by a methoxy group as a vertical direction are more stable than those substituted by a methoxy group as a horizontal direction.

In the 6- and 7-membered cyclic compounds, the potential energies of 5-methoxy-1-methylenecyclohexane and 6-methoxy-1-methylenecycloheptane are more stable than

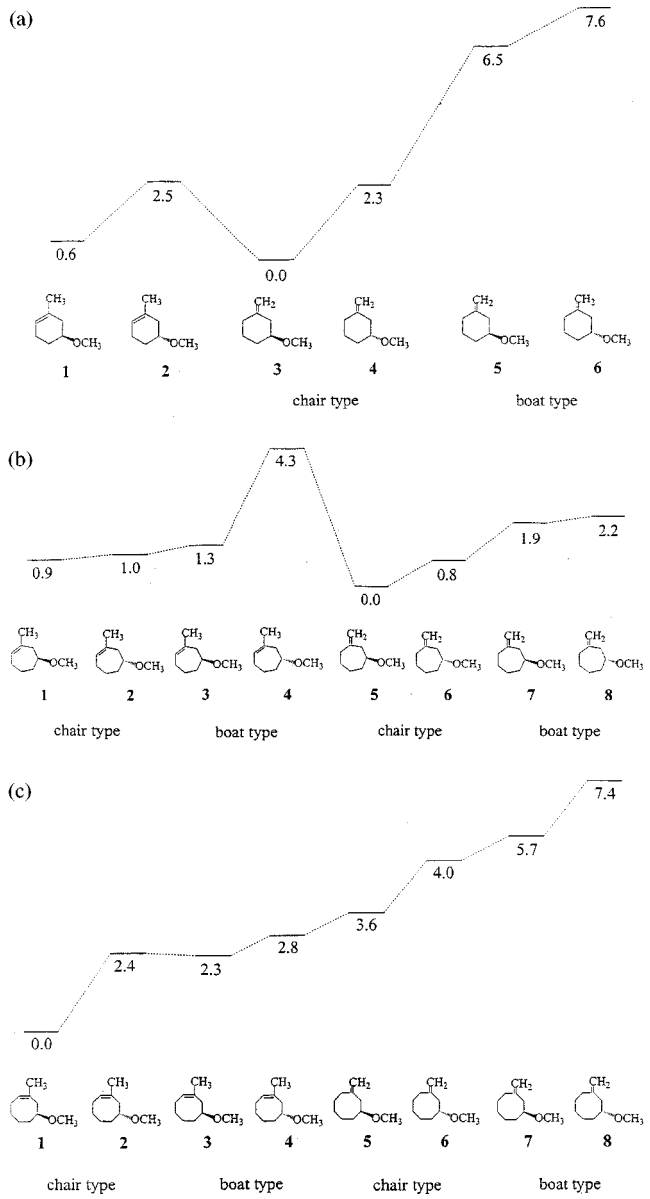

Figure 1. Three schematic potential energy diagrams and optimized structures of the structural isomers of the 6-, 7-, and 8-membered cyclic compounds at the MP2/6-311+G** level. (a): Relative potential energies of the 6-membered cyclic compounds. (b): Relative potential energies of the 7-membered cyclic compounds. (c): Relative potential energies of the 8-membered cyclic compounds. All energies are adiabatic values and are in units of kcal/mol.

those of 5-methoxy-1-methylcyclohexene and 6-methoxy-1-methyl-cycloheptene by 0.6 and 0.9 kcal/mol, respectively. Meanwhile, in the 8-membered cyclic compound, 7-methoxy-1-methylcyclooctene is more stable than 7-methoxy-1-methylenecyclooctane by 3.6 kcal/mol. The relative energy difference (3.6 kcal/mol) between 7-methoxy-1-methylcyclooctene and 7-methoxy-1-methylenecyclooctane is four times larger than those (0.6 and 0.9 kcal/mol) of the 6- and 7-membered rings. By the experimental results,[1-10] methylcyclohexene and methylenecyclohexane of 6-membered cyclic products are cyclized from the acetals with an allylsilane group and the acyclic substrates. While, in the 8-membered ring, the acetals with an allylsilane group only cyclized to methylcyclooctene. Our results for the relative stability are in line with the experimental[1-10] and theoretical[12-16] results.

Conclusionally, the relative potential energies of the 6- and 7-membered cyclic products with an exocyclic double bond are similar to those of the methylcycloalkene products with a double bond on the cyclic frame. The potential energy differences between the methylcycloalkene and methylenecycloalkane products are very small (0.6 kcal/mol for 6-membered ring and 0.9 kcal/mol for 7-membered ring). Due to small energy differences between methylcyclohexenes and methylenecyclohexanes, both products can be formed from acyclic substrates. Whereas, in the 8-membered cyclic product, the potential energies of the methylcyclooctenes are much lower than those of the methylenecyclooctanes. The energy difference between two isomeric products is 3.6 kcal/mol. A more stable 7-methoxy-1-methylcyclooctene is formed from the acyclic substrates. As a result, the olefinic cyclizations produced from the acyclic substrates with an allylsilane group may be greatly depended on the relative stability for the structural isomers of the fused-ring products.

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References

1. van der Gen, A.; Wiedhaup, K.; Swoboda, J. J.; Dunathan, H. C.; Johnson, W. S. *J. Am. Chem. Soc.* **1973**, *95*, 2656.
2. Fleming, I.; Pearce, A. *J. Chem. Soc. Perkin Trans. I* **1981**, 251.
3. Fleming, I.; Paterson, I.; Pearce, A. *J. Chem. Soc. Perkin Trans. I* **1981**, 256.
4. Chow, H.-F.; Fleming, I. *J. Chem. Soc. Perkin Trans. I* **1984**, 1815.
5. Baldwin, J. E.; Lusch, M. J. *Tetrahedron* **1982**, *38*, 2939.
6. Wang, D.; Chan, T.-H. *J. Chem. Soc. Chem. Commun.* **1984**, 1273.
7. (a) Lee, T. V.; Roden, F. S.; Yeoh, H. T.-L. *Tetrahedron Lett.* **1990**, *31*, 2063. (b) Lee, T. V.; Roden, F. S.; Yeoh, H. T.-L. *Tetrahedron Lett.* **1990**, *31*, 2067.
8. Kang, K.-T.; Park, D. K.; Lee, S. J.; Sung, T. M. *Bull. Korean Chem. Soc.* **1996**, *17*, 777.
9. Sung. T. M.; Kwak, W. Y.; Kang, K.-T. *Bull. Korean Chem. Soc.* **1998**, *19*, 862.
10. Barbero, A.; Carcia, C.; Pulido, F. J. *Tetrahedron* **2000**, *56*, 2739.
11. Frish, M. J.; Trucks, G. W.; Head-Gordon, M. H.; 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 94*; Gaussina Inc.: Pittsburgh, PA, 1995.
12. Deleris, G.; Pillot, J. P.; Rayez, J. C. *Tetrahedron* **1980**, *36*, 2215.
13. Frenking, G.; Köhler, K. F.; Reetz, M. T. *Angew. Chem. Int. Engl.* **1991**, *30*, 1146.
14. Maeta, H.; Nagasawa, T.; Handa, Y.; Takei, T.; Osamura, Y.; Suzuki, K. *Tetrahedron Lett.* **1995**, *36*, 899.
15. (a) Hudec, J.; Huke, J.; Liebeschuetz, J. W. *J. Chem. Soc. Perkin Trans. II* **1998**, 1129. (b) Hudec, J.; Huke, J.; Liebeschuetz, J. W. *J. Chem. Soc. Perkin Trans. II* **1998**, 1139.
16. Kantorowski, E. J.; Eisenberg, S. W. E.; Fink, W. H.; Kurth, M. J. *J. Org. Chem.* **1999**, *64*, 570.