

# Transition Structures for [2,3]-Wittig Rearrangement

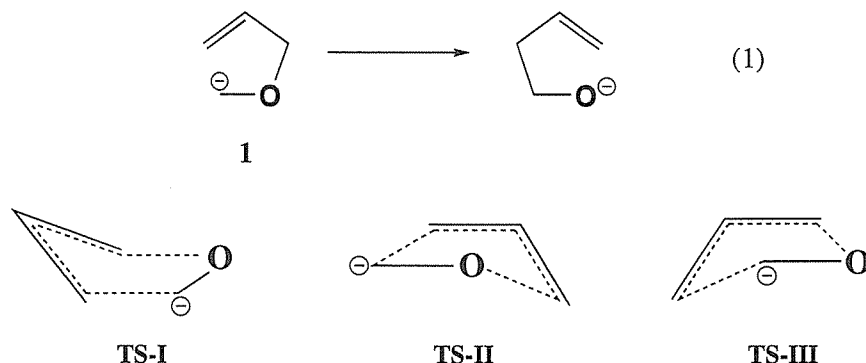
—Substitution Effect—

Toshiya OKAJIMA

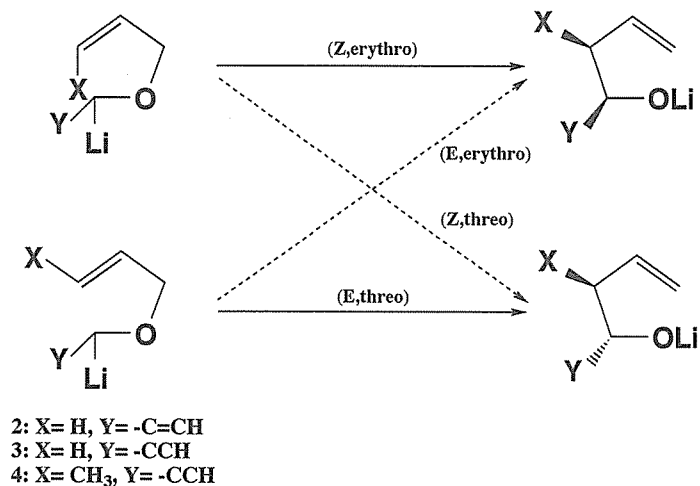
**Abstract:** The transition structures for [2,3]-Wittig rearrangement of allyloxymethyl lithium (2 having vinyl group (-CH=CH<sub>2</sub>) at C1, 3 having -CCH group at C1, and 4 having -CCH at C1 and methyl at C5 position) have been located at the RHF/3-21G basis set. Energies of all stationary points, including reactants, transition structures, and products, located at the RHF13-21G basis set, were evaluated at the second order Moller-Plesset correlation level with the 6-31(+)\*G(\*) basis sets.

## Introduction

[2,3]-Wittig rearrangement (eq. (1), Figure 1) is one of the useful tool to construct the carbon-carbon bond and has been an efficient method for acyclic stereocontrol. The mechanism of [2,3]-Wittig rearrangement has been the subject of controversy which has recently lead to consensus.<sup>1</sup> Recent *ab initio* calculations indicates that the Rautenstrach's type concerted transition structure (TS-I) is considered to be the most plausible one for the parent reaction of allyloxymethyl lithium (1). However the activation barrier for the stepwise mechanism proceeding through Trost's envelop (TS-II) is almost the same with that of TS-I. The Nakai's type transition structure (TS-III) is energetically highest at all MP2/6-31(+)\*G(\*) levels based on the RHF/3-21G basis set (Figure 1). The TS-I is concerted and more synchronous than TS-II and TS-III which have almost the complete O2-C3 single bond even at transition state. The stability of TS-II is enhanced by the formation of an internal Coulomb interaction between Li atom and C4 atom. In continuation of the study of [2,3]-Wittig rearrangement, the author has extended the investigations to the stereoselection for [2,3]-



**Figure 1.** Three transition-state models (Rautenstrach's type (TS-I), Trost's type (TS-II), and Nakai's type (TS-III) for [2,3]-Wittig rearrangement (eq. 1).)



Scheme 1.

Wittig rearrangement of C1- and/or C5-substituted allyloxymethyl lithium derivatives (Scheme 1) by *ab initio* molecular orbital calculation.

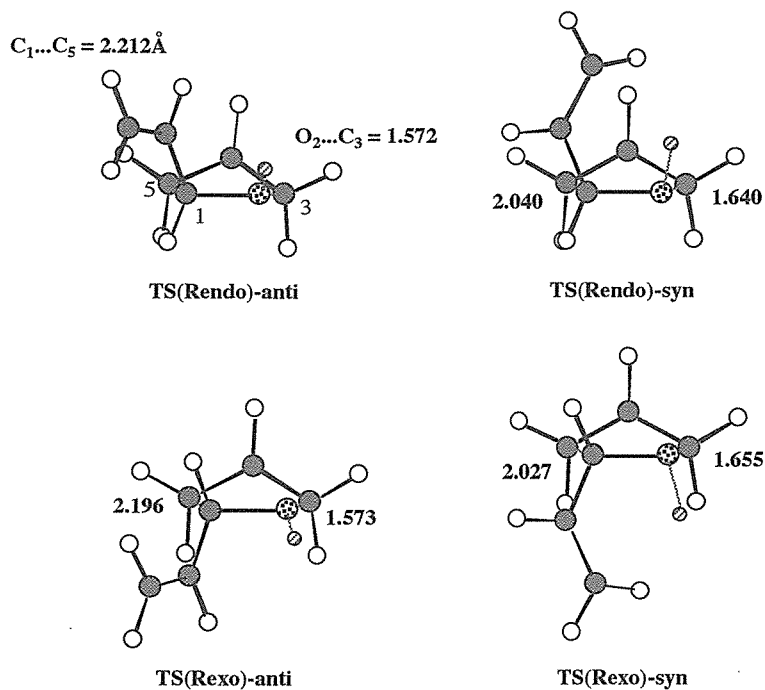
There is diastereoselectivity with respect to the chiral centers formed at the termini of the new C-C bond. A *Z* substrate generally exhibits erythro selection, while an *E* substrate leads to threo selectivity.

### Computational Details

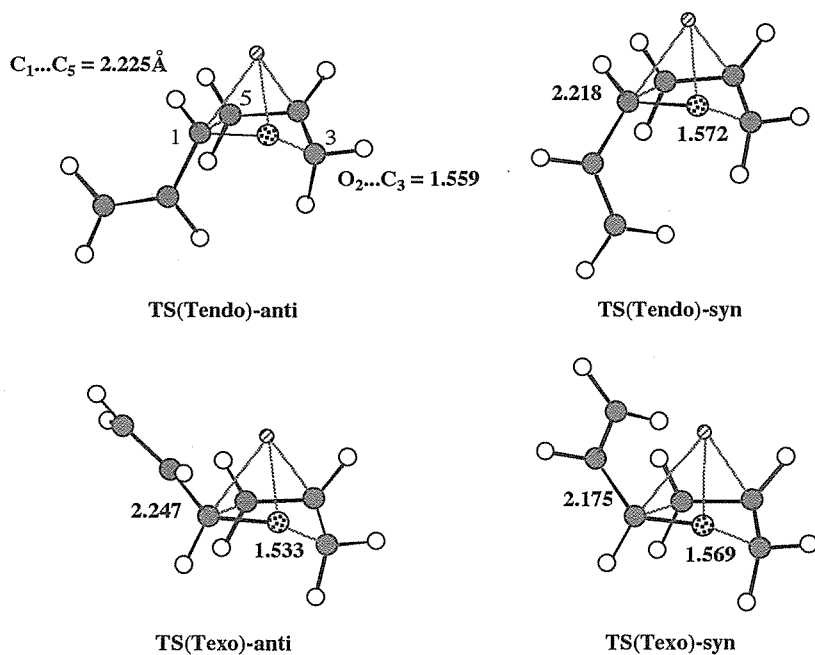
*Ab initio* molecular orbital calculations were carried out using the Gaussian 94 suite of programs.<sup>2</sup> The geometry optimizations and frequency analysis were computed at the RHF/3-21G basis set using SGI-INDY workstations. All transition structures have a single imaginary frequency. Single-point energies were evaluated at MP2(fc)/6-31(+)\*G(\*) level of theory<sup>3</sup> based on RHF/3-21G geometries. The split valence 6-31(+)\*G(\*) basis set includes diffuse functions, denoted by +, and d-polarization functions, denoted by an asterisk (\*). Diffuse functions are desired for proper description of the anionic lobe at C1 atom.

### Results and Discussion

In transition structures for the rearrangement of **2**, two orientations of vinyl side chain at C1-position is possible. These are labeled as syn and anti as shown in Figure 2-1 and 2-2. In Table 1, the total energies of eight possible transition structures are presented. The transition structure (**TS (Rendo)-syn**) is the most stable in four transition structures having Rautenstrach's envelop (**I**) and **TS (Texo)-syn** is the most stable in four transition structures having Trost's envelop (**II**). The geometries of the transition structures remains approximately constant as compared with those of parent **TS-I** or **TS-II** shown in Figure 1. The C1...C5 atomic distances are in the small range of 2.0 ~ 2.3 Å and those of O2...C3 are 1.5 ~ 1.7 Å. The transition structures having the coordination geometry of Li to  $\pi$ -orbital of vinyl substituent (syn transition structures) have generally shorter distances of C1...C5 incipient forming bond. In the syn structure **TS (Tendo)-syn**, the coordination of



**Figure 2-1.** Four transition structures having Rautenstrach's envelop for [2, 3]-Wittig rearrangement of 2.



**Figure 2-2.** Four transition structures having Trost's envelop for [2, 3]-Wittig rearrangement of 2.

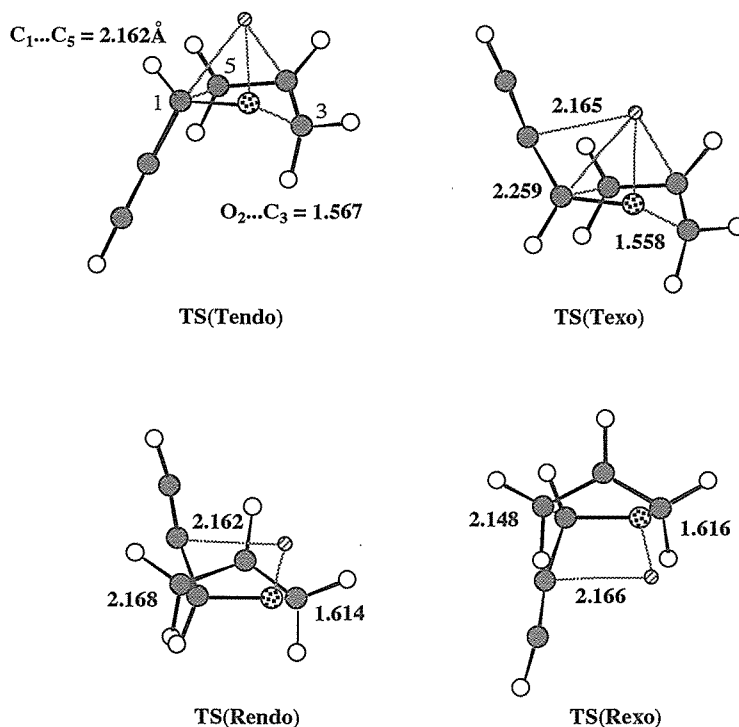
**Table 1.** The Relative energies (kcal/mol, //RHF/3-21G) of [2,3]-Wittig rearrangement of **2**.<sup>a</sup>

calcn. level	TS(Rendo)		TS(Rexo)		TS(Tendo)		TS(Texo)	
	anti	syn	anti	syn	anti	syn	anti	syn
MP2/6-31G	+15.9	0.0	+17.2	+2.5	+17.7	+15.4	+16.4	+4.2
MP2/6-31+G	+14.6	0.0	+15.7	+2.0	+19.9	+17.6	+20.0	+8.3
MP2/6-31G*	+17.2	0.0	+18.6	+2.6	+15.2	+12.5	+13.2	+1.1
MP2/6-31+G*	+16.3	0.0	+17.4	+2.2	+16.9	+14.1	+16.1	+2.1

a)  $\Delta\Delta E^\ddagger = \Delta E^\ddagger(\text{TS}(X)-Y) - \Delta E^\ddagger(\text{TS}(\text{Rendo})-\text{syn})$   
 (X=Rendo, Rexo, Tendo, and Texo, Y=anti and syn)

Li atom to vinyl group does not occur. The energy difference between anti and syn structures in **TS(Tendo)** is in the range of only 2 ~ 3 kcal/mol, though those are >12 kcal/mol for the other three transition structures (**TS(Rendo)**, **TS(Rexo)**, and **TS(Texo)**). This is because of the lacking of the stabilization attributing to Li... $\pi$  Coulomb interaction in **TS(Tendo)**-syn.

For the rearrangement of **3** having -CCH group at C1-position, three transition structures (**TS(Texo)**, **TS(Rendo)**, and **TS(Rexo)**) have the coordination geometries between Li atom and -CCH group. Only **TS(Tendo)** has no interaction between them. (Figure 3) **TS(Rendo)** having Rautenstrach's envelop, is the most favorable among four transition structures, except for the energetic at MP2/6-31G\* level. (Table 2) **TS(Tendo)** is the most unfavorable among the four transition structures. As shown in Table 2, the relative energies for the rearrangement of **3**, indicating that the energy difference between **TS(Rendo)** and **TS(Tendo)** is several kcal/mol, whereas those for

**Figure 3.** The transition structures for [2, 3]-Wittig rearrangement of **3**.

**Table 2.** The Relative energies (kcal/mol, //RHF/3-21G) of [2,3]-Wittig rearrangement of **3**.<sup>a</sup>

calcn. level	TS(Rendo)	TS(Rexo)	TS(Tendo)	TS(Texo)
MP2/6-31G	0.0	+1.1	+6.7	+0.7
MP2/6-31+G	0.0	+0.8	+9.8	+5.0
MP2/6-31G*	0.0	+1.0	+4.5	-3.3
MP2/6-31+G*	0.0	+0.7	+6.7	+0.0

a)  $\Delta\Delta E^* = \Delta E^*(\text{TS}(X)) - \Delta E^*(\text{TS}(\text{Rendo}))$  (X=Rexo, Tendo, and Texo)

**TS(Rexo)** and **TS(Texo)** are in the range of only 2 ~ 3 kcal/mol. With the MP2/6-31G\* level, **TS(T-exo)** was more favored than **TS(Rendo)**, which was previously pointed out that the polarization function (\*) included in energy evaluation makes Trost's type transition structure more favorable than Rautenstrach's one.<sup>1</sup> This is because that polarization function tends to stabilize multi-centered interaction seen in Trost's type transition structure, in which Li cation coordinates three atoms (C1, O2, and C4) in the envelop structure (for Rautenstrach's type, only two atoms (C1 and O2) interacts with Li cation).

For [2, 3]-Wittig rearrangement of **4**, the eight transition structures could be located. Figure 4-1 shows four Rautenstrach's type transition structures and Figure 4-2 Trost's type ones. The most stable transition structure is **TS(Rendo)** for both cis and trans substrates. The stabilization of **TS(Texo)** is attributable to the inclusion of polarization function for energy calculation. Table 3 shows the relative energies between these transition structures. **TS(Tendo)** are relatively unstable due to the lacking of Coulomb stabilization for both cis and trans substrates.

As shown in Figure 5, for cis substrates **TS(Tendo)** and **TS(Rexo)** give the major (Z,erythro) stereoisomeric products and **TS(Texo)** and **TS(Rendo)** minor (Z,threo) stereoisomers. For trans substrates, **TS(T-endo)** and **TS(Rexo)** lead to the major (E,threo) products. Figure 5 summarizes the substitution pattern to give erythro and threo products by substituting each endo and exo hydrogen at C1 atom.

Interestingly, for Rautenstrach's type transition structure, Li cation can move to coordinate to  $\pi$ -electrons of vinyl or -CCH group for both exo and endo structures, whereas in Trost's type transition structure, only when Li cation locates on the same side of these C1-substituents with respect to the average plane of five-membered envelop, the coordination between Li and  $\pi$  occurs. For example, in Figure 3, although **TS(Texo)** having Li and -CCH group positioned on the same side of the envelop to lead the coordination structure, in **TS(Tendo)** having those on the opposite side of the envelop, the coordinating structure is not possible. On the other hand, both Rautenstrach's type transition structures **TS(Rendo)** and **TS(Rexo)** have coordination structure. In parent **TS-I** (Figure 1), Li cation locates just on the plane formed by four atoms (C1, O2, O4, and C5) in the envelop. In these two transition structures, Li atom can move to coordinate with triple bond to obtain maximum Coulomb stabilization from the plane.

### Summary

The present study indicates that [2, 3]-Wittig rearrangement of **2-4** proceeds through the most

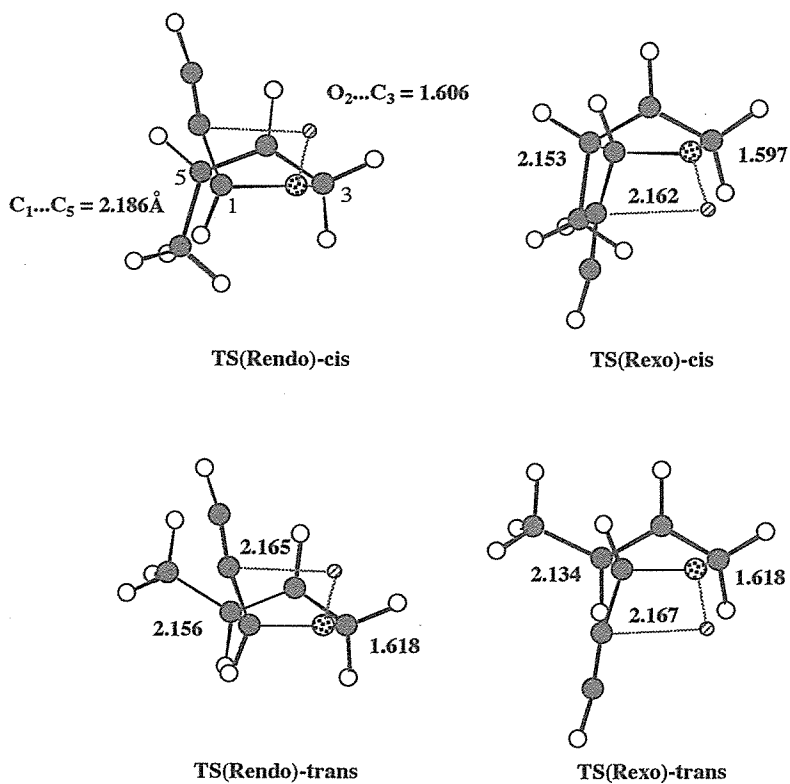


Figure 4-1. Four transition structures having Rautenstrach's envelop for [2, 3]-Wittig rearrangement of 4.

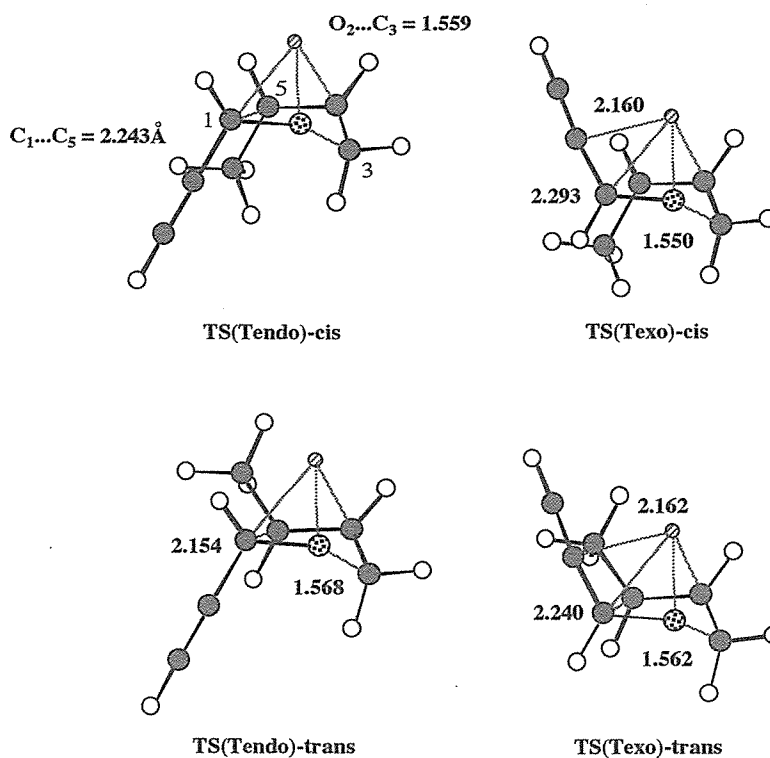


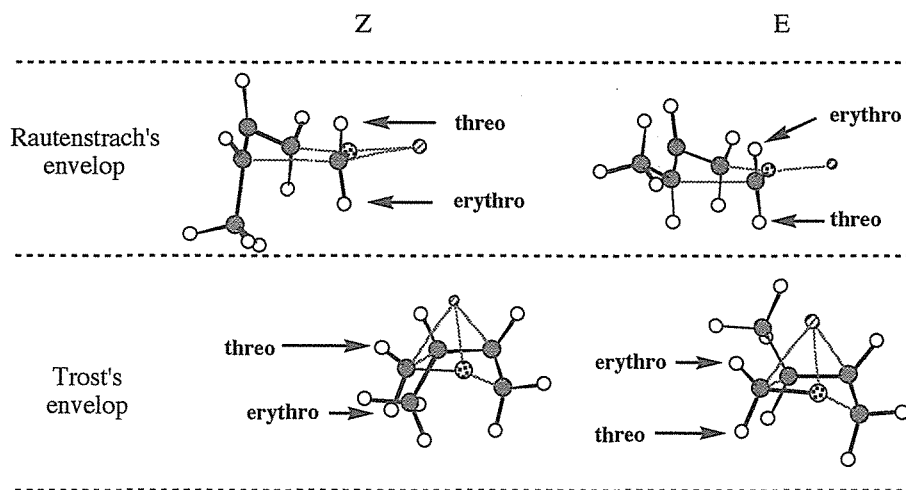
Figure 4-2. Four transition structures having Trost's envelop for [2, 3]-Wittig rearrangement of 4.

**Table 3.** The Relative energies (kcal/mol, //RHF/3-21G) of [2,3]-Wittig rearrangement of **4**.<sup>a</sup>

calcn. level	cis			
	TS(Rendo)	TS(Rexo)	TS(Tendo)	TS(Texo)
MP2/6-31G	0.0	+1.7	+ 9.7	+1.0
MP2/6-31+G	0.0	+1.4	+13.0	+5.5
MP2/6-31G*	0.0	+1.5	+ 7.2	-3.0
MP2/6-31+G*	0.0	+1.3	+ 9.6	+0.5
calcn. level	trans			
	TS(Rendo)	TS(Rexo)	TS(Tendo)	TS(Texo)
MP2/6-31G	0.0	+1.0	+ 7.8	+0.7
MP2/6-31+G	0.0	+0.7	+10.7	+4.8
MP2/6-31G*	0.0	+1.0	+ 5.5	-3.2
MP2/6-31+G*	0.0	+0.8	+ 7.6	-0.1

a)  $\Delta\Delta E^* = \Delta E^*(\text{TS}(X-Y)) - \Delta E^*(\text{TS}(\text{Rendo}-Y))$   
 (X=Rendo, Rexo, Tendo, and Texo, Y=cis and trans)

TS(Tendo)-cis, TS(Rexo)-cis	—————→	Z, erythro
TS(Texo)-cis, TS(Rendo)-cis	—————→	Z, threo
TS(Tendo)-trans, TS(Rexo)-trans	—————→	E, threo
TS(Texo)-trans, TS(Rendo)-trans	—————→	E, erythro

**Figure 5.** The stereoselectivity for [2,3]-Wittig rearrangement of **3**.

stable Rautenstrach's type transition structure (**TS-I**) rather than the Trost's type (**TS-II**), though energies evaluated including polarization function suggests **TS-II** is more stable than **TS-I**. Of course, solvation of etheral solvent at Li cation may significantly affect the stability of the transition structures. For example, the transition structure having Li...alkenyl (alkynyl) interaction may become unimportant for stereoselectivity, because that the weak interaction between Li and  $\pi$ -electrons may be cleaved by the coordination of the etheral oxygen atom. The investigation on the

**Table 4.** The energetics (a. u. //RHF/3-21G) of [2,3]-Wittig rearrangement of **2**.

calcn. level	TS(Rendo)-anti	TS(Rendo)-syn	TS(Rexo)-anti	TS(Rexo)-syn
MP2/6-31G	-315.172551	<b>-315.197849</b>	-315.170492	-315.193876
MP2/6-31+G	-315.201619	<b>-315.224919</b>	-315.199929	-315.221714
MP2/6-31G*	-315.589716	<b>-315.617076</b>	-315.587390	-315.612944
MP2/6-31+G*	-315.614929	<b>-315.640984</b>	-315.613167	-315.637504
calcn. level	TS(Tendo)-anti	TS(Tendo)-syn	TS(Texo)-anti	TS(Texo)-syn
MP2/6-31G	-315.169624	-315.173268	-315.171631	<b>-315.191149</b>
MP2/6-31+G	-315.193154	-315.196915	-315.193072	<b>-315.211659</b>
MP2/6-31G*	-315.592804	-315.597109	-315.595979	<b>-315.618889</b>
MP2/6-31+G*	-315.614090	-315.618464	-315.615364	<b>-315.637569</b>

**Table 5.** The energetics (a. u. //RHF/3-21G) of [2,3]-Wittig rearrangement of **3**.

calcn. level	TS(Rendo)	TS(Rendo)	TS(Texo)	TS(Texo)
MP2/6-31G	<b>-313.975999</b>	-313.974212	-313.965282	-313.974924
MP2/6-31+G	<b>-314.003708</b>	-314.002490	-313.988093	-313.995716
MP2/6-31G*	-314.387265	-314.385695	-314.380038	<b>-314.392522</b>
MP2/6-31+G*	<b>-314.411679</b>	-314.410531	-314.400933	-314.411646

**Table 6.** The energetics (a. u. //RHF/3-21G) of [2,3]-Wittig rearrangement of **4**.

calcn. level	TS(Rendo)-cis	TS(Rexo)-cis	TS(Tendo)-cis	TS(Rexo)-cis
MP2/6-31G	<b>-353.086550</b>	-353.083879	-353.071122	-353.084948
MP2/6-31+G	<b>-353.116614</b>	-353.114412	-353.095885	-353.107834
MP2/6-31G*	-353.554171	-353.551771	-353.542756	<b>-353.558931</b>
MP2/6-31+G*	<b>-353.580440</b>	-353.578376	-353.565124	-353.579672
calcn. level	TS(Rendo)trans	TS(Rexo)-trans	TS(Tendo)-trans	TS(Texo)-trans
MP2/6-31G	<b>-353.091022</b>	-353.089394	-353.078653	-353.089941
MP2/6-31+G	<b>-353.120729</b>	-353.119626	-353.103688	-353.113085
MP2/6-31G*	-353.558458	-353.556933	-353.549633	<b>-353.563634</b>
MP2/6-31+G*	-353.584552	-353.583285	-353.572419	<b>-353.584687</b>

solvent effect has been going on.

### Acknowledgment

The author thanks the Information Processing Center of Saga University for the use of Power Indigo2 work station.

### References and Notes

- 1) Okajima, T. *Nippon Kagaku Kaishi*, **1997**, 529.
- 2) Gaussian 94, Revision D.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.



- 3) (1) **diffusion function (+)**: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. (2) **6-31+G\***: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (3) **MP2**: (a) Krishnan, R.; Frish, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244. (b) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561. (c) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *S10*, 1. (d) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.