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Transiti[1]on Structures for the Aromatic Claisen Rearrangements by the Molecular Orbital Method

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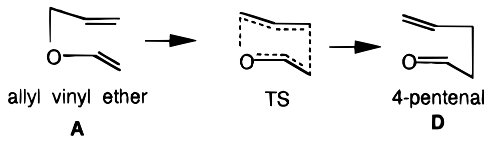
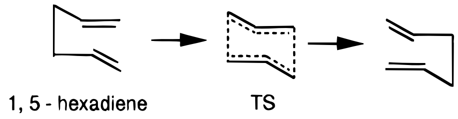
Ab initio calculations were performed for eight Claisen rearrangements, eqs 1−8. Transition-state (TS) structures of [3,3] sigmatropic rearrangements of reactions 1−4 are similar, but their activation energies (E_a's) are different, $E_a(1) < E_a(2)$ and $E_a(3) < E_a(4)$. From the intermediate of reaction 3, a hydrogen is moved intermolecularly to form the product, *o*-allyl phenol. The lower reactivities of reactions 2 and 4 relative to reactions 1 and 3 are ascribed to large endothermicities in the sigmatropic rearrangements, respectively. Chair-type transition states are more favorable than boat-type transition states in reactions 1−4. The allyl group is released from the in-plane C−X (X = O or N) σ bond and is captured by the π-type lone-pair electrons. The sulfur- and phosphorus-containing rearrangements, reactions 5−8, are computed to have smaller activation energies but are to be less exothermic than those of oxgyen- and nitrogen-containing rearrangements.

I. Introduction

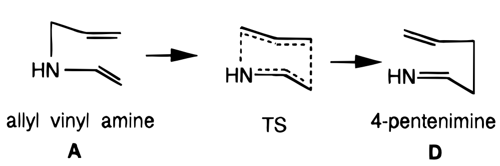
The simplest example of a Claisen rearrangement is the thermal conversion of allyl vinyl ether to 4-pentenal.[1,2] Reliable predictions of the stereochemical features of the Claisen rearrangement can be made on the basis of the preference for a chairlike transition state (TS).[3] Ab initio calculations have shown that the chairlike TS is 6.6 kcal/mol more stable than the boatlike TS, with MP2/6-31G*//RHF/3-21G.[4a] 1,5-Hexadiene is isoelectronic with allyl vinyl ether and undergoes the Cope rearrangement.[5]



[1]

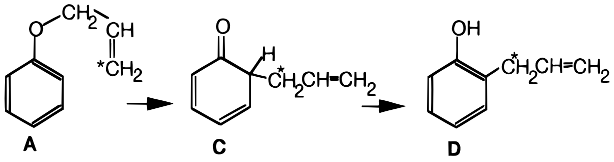


Thus, it is of theoretical interest to determine whether the isoelectronic allylvinylamine can cause the Claisen ("amino-Claisen") rearrangement.



[2]

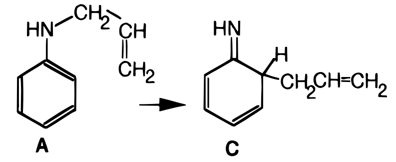
Although reaction 2 is not known, with three methyl substituents the reaction is quite facile.[6] Extensive studies of Claisen rearrangements of allyl ethers of phenols have provided evidence pertaining to [3,3]-sigmatropic rearrangements. An important clue regarding the mechanism of the Claisen rearrangement was obtained by use of ^{14}C-labeled allyl phenyl ether.[7]



[3]

The intramolecular nature of the rearrangement was established by a crossover experiment. Two allyl aryl ethers were heated together, and the reaction was found to yield the same products as when they were heated independently.[8] The rearrangement proceeds without solvents.

In contrast to the facile occurrence of reaction 3, the isoelectronic substrate *N*-allylaniline is known to not rearrange under the standard condition,[9a] and the following amino-Claisen reaction (4) requires high temperature.[9b] The role of second-row heteroatoms, sulfur and phosphorus, in Claisen rearrangements is of



[4]

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Claisen, L. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3157.

(2) Schuler, F. W.; Murphy, G. W. *J. Am. Chem. Soc.* **1950**, *72*, 3155.

(3) (a) Marber, R.; Saucy, G. *Helv. Chim. Acta* **1967**, *50*, 2095. (b) Burgstahler, A. W. *J. Am. Chem. Soc.* **1960**, *82*, 4681. (c) Rhoads, S. J. In *Molecular Rearrangements*; de Mayo, P., Ed.; Wiley-Interscience, New York, 1963; Vol. 1, p 655.

(4) (a) Vance, R. L.; Rondon, N. G.; Houk, K. N.; Jensen, F.; Borden, W. T.; Komornichi, A.; Wimmer, E. *J. Am. Chem. Soc.* **1988**, *110*, 2314. (b) Yoo, H. Y.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 12047.

(5) Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 441.

(6) Hill, R. K.; Gilman, N. W. *Tetrahedron Lett.* **1967**, 1421.

(7) Ryan, J. P.; O'Connor, P. R. *J. Am. Chem. Soc.* **1952**, *74*, 5866.

(8) Hurd, C. D.; Schmerling, L. *J. Am. Chem. Soc.* **1937**, *59*, 107.

(9) (a) Rhoads, S. J.; Raulins, N. R. In *Organic Reactions*; Dowben, W. G., Ed.; Wiley: New York, 1975; Vol. 22, p 1. (b) Jolidon, S.; Hansen, H.-J. *Helv. Chim. Acta* **1977**, *60*, 978.

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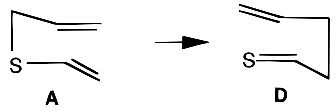
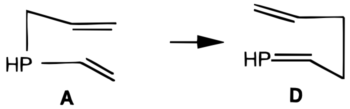
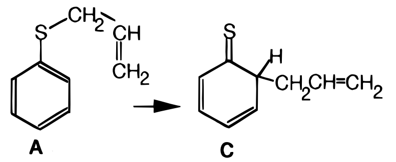
mechanistic concern. These atoms have large C−X distances and appear to be more vulnerable to rearrangements than oxygen and nitrogen atoms.



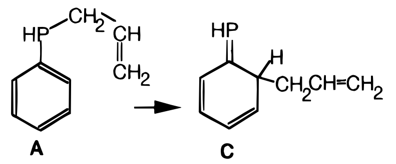
[5]



[6]



[7]



[8]

In the current study, eight reactions, 1−8, are compared theoretically. This comparison may elucidate the best condition for the Claisen rearrangement. The first interest is in the difference elicited by vinyl (reactions 1 and 2) and phenyl (reactions 3 and 4) groups. The second is in the role of heteroatoms (oxygen, nitrogen, sulfur, and phosphorus). For instance, average C−O and C−N bond energies are 88 and 73.2 kcal/mol, respectively. Since the C−N bond is cleaved more readily than the C−O bond, the contrast between the ready occurrence of reaction 3 and the high-temperature requirement of reaction 4 is curious. The third interest is in the isomerization step **C** → **D** in reaction 3. In ketone **C**, the C−H bond must be broken to arrive at the phenol **D**. This step needs to be clarified so as to understand thoroughly the reaction mechanism for allyl aryl ethers. Transition states of eight reactions are examined with various computational methods, and the similarities and differences are examined. Which is the best heteroatom among O, NH, S and PH for the Claisen rearrangement?

II. Method of Calculations

Ab initio geometry optimizations with RHF/3-21G, RHF/6-31G*, and Becke3LYP/6-31G*[10] (reactions 1−8) and CISD/6-31G* (reactions 1 and 2) were carried out using GAUSSIAN 92[11] and GAUSSIAN92/DFT.[12] Single-point calculations (frozen core), MP2/6-31G*//RHF/3-21G, MP2/6-311G**//RHF/6-31G* (reactions 1−4) and MP4(SDTQ)/6-31G*//RHF/3-21G (reactions 1 and 2) were also made to refine the obtained activation energies. Mass-weighted intrinsic reaction coordinates (IRCs) of reactions 3 and 4 were searched for using the method of Gonzalez and Schlegel,[13] with RHF/3-21G. All the ab initio calculations were performed on the CONVEX C-220 computer at the Information Processing Center of Nara University of Education and the Personal Iris 4D/35 computer at Matsushita Electric Works, Ltd.

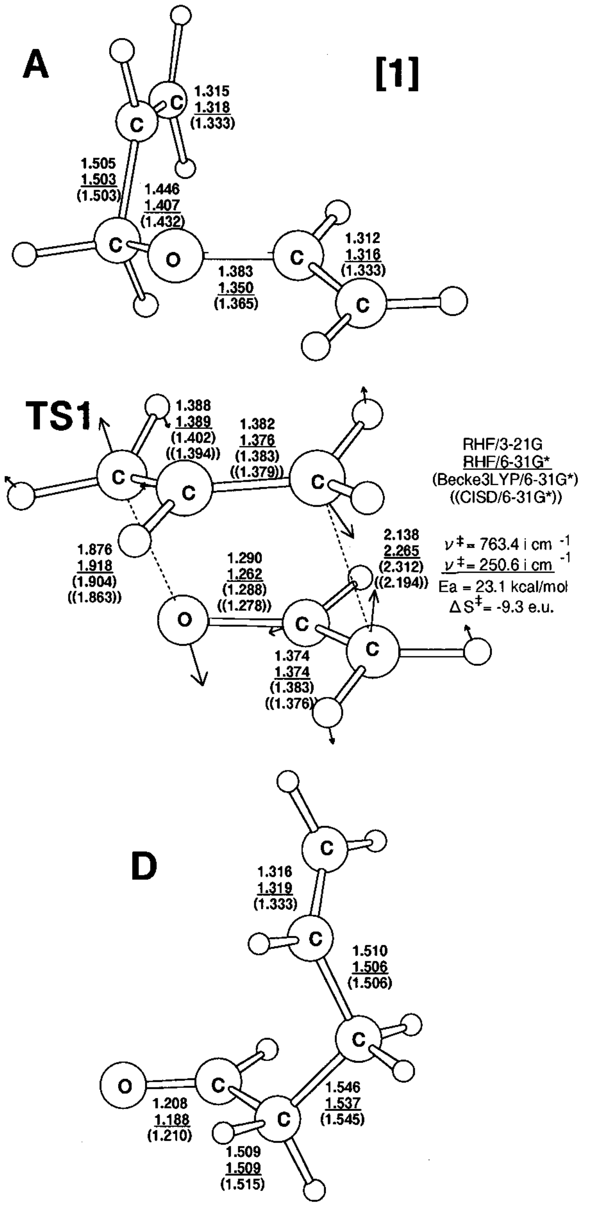


Figure 1. Geometries of reactant (allyl vinyl ether, **A**), TS (**TS1**), and product (4-pentenal, **D**) of reaction 1. Empty circles stand for hydrogen atoms. Distances are in Å. For TS, RHF/3-21G, RHF/6-31G* (underlined), (Becke3LYP/6-31G*), and ((CISD/6-31G*)) distances are shown. The reaction-coordinate vector corresponding to the sole imaginary frequency ($\nu^{\ddagger}$ = 763.4i cm^{-1} with RHF/3-21G) is sketched. The activation energy, E_a, is calculated by the single-point energy by MP2/6-31G* on the RHF/3-21G geometry, MP2/6-31G*//RHF/3-21G. The activation entropy, $\Delta S^{\ddagger}$, is by RHF/3-21G.

III. Results of Calculations and Discussion

Figure 1 shows three geometries for reaction 1, for which RHF/3-21G and RHF/6-31G* data of **TS1** were already reported.[4] The electron-correlation effect is found

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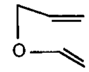
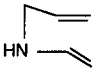
(10) Becke, A. D. *J. Chem.* **1993**, *98*, 5648.

(11) 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. *Gaussian92, Revision C*, Gaussian, Inc., Pittsburgh, PA, 1992.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; 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. *Gaussian92/DFT, Revision G.4*, Gaussian, Inc., Pittsburgh, PA, 1992.

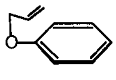
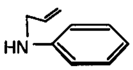
(13) (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

Table 1. Total Energies in Atomic Units by Various Methods for Reactions 1 and 2[a]

Reaction	Methods	**A** (reactant)	**TS1**	**D** (product)
reaction [1] Figure 1 	RHF/3-21G	-267.303723 (0)	-267.238586 (40.9)	-267.324536 (-13.1)
	RHF/6-31G*	-268.793473 (0)	-268.717659 (47.6)	-268.827377 (-21.3)
	Becke3lyp/ 6-31G*	-270.504747 (0)	-270.461127 (27.4)	-270.533432 (-18.0)
	CISD/6-31G*		-269.432976	
	MP2/6-311G**// RHF/6-31G*	-269.777207 (0)	-269.738428 (24.3)	-269.814577 (-23.5)
	MP2/6-31G*// RHF/3-21G	-269.598949 (0)	-269.562130 (23.1)	-269.636600 (-23.6)
	MP3/6-31G*// RHF/3-21G	-269.639732 (0)	-269.585340 (34.1)	-269.673776 (-21.4)
	MP4/6-31G*// RHF/3-21G	-269.682613 (0)	-269.640543 (26.4)	-269.719011 (-22.8)
reaction [2] Figure 2 	RHF/3-21G	-247.589144 (0)	"cis" -247.512261 (48.2) "trans" -247.506846 (51.6)	-247.590793 (-1.0)
	RHF/6-31G*	-248.969012 (0)	"cis" -248.883159 (53.9)	-248.983698 (-9.2)
	Becke3lyp/ 6-31G*	-250.643551 (0)	"cis" -250.591659 (32.6)	-250.654942 (-7.1)
	CISD/6-31G*		"cis" -249.592740	
	MP2/6-311G**// RHF/6-31G*	-249.934265 (0)	"cis" -249.881657 (33.0)	-249.939201 (-3.1)
	MP2/6-31G*// RHF/3-21G	-249.760467 (0)	"cis" -249.719418 (25.8) "trans" -249.714460 (28.9)	-249.778685 (-11.4)
	MP3/6-31G*// RHF/3-21G	-249.806583 (0)	"cis" -249.748366 (36.5)	-249.824944 (-11.5)
	MP4/6-31G*// RHF/3-21G	-249.847384 (0)	"cis" -249.800551 (29.4)	-249.866506 (-12.0)

[a] Values in parentheses denote stabilizing (<0) or destabilizing (>0) energies (in kcal/mol) relative to those of reactants **A**

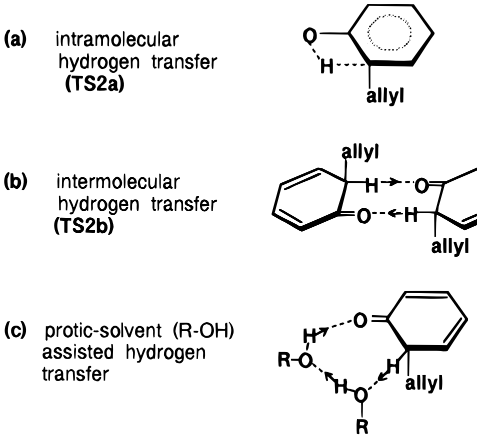
Table 2. Total (in au) and Relative (in kcal/mol) Energies of Reactions 3 and 4

Reaction	Methods	**A** (reactant)	**TS1**	**C** (intermediate)	**TS2a**	**TS2b**	**D** (product)
reaction [3] Figures 3 and 4 	RHF/3-21G	-419.123969 (0) -419.121873 (1.3) *	"chair" -419.04 84 (51.7) "boat" -419.032595 (57.3)	-419.094646 (18.4)	-418.971333 (95.8)	-838.159748 (55.3)	-419.133751 (-6.1)
	RHF/6-31G*	-421.461762 (0)	"chair" -421.372573 (56.0)	-421.446892 (9.3)	-421.320800 (88.5)		-421.473148 (-7.1)
	Becke3lyp/ 6-31G*	-424.163447 (0)	"chair" -424.105352 (36.5)	-424.143383 (12.6)	-424.054158 (68.6)		-424.175683 (-7.7)
	MP2/6-311G**// RHF/6-31G*	-423.016849 (0)	"chair" -422.964854 (32.6)	-422.982931 (21.3)	-422.915186 (63.8)		-423.042895 (-16.3)
	MP2/6-31G*// RHF/3-21G	-422.770868 (0) -422.768799 (1.3) *	"chair" -422.719459 (32.3) "boat" -422.709629 (38.4)	-422.754867 (10.0)	-422.661690 (68.5)	-845.489878 (32.5)	-422.789449 (-11.7)
reaction [4] Figure 5 	RHF/3-21G	-399.405042 (0)	"cis" -399.307173 (61.4) "trans" -399.302832 (64.1)	"cis" -399.356541 (30.4) "trans" -399.356203 (30.6)	-399.243626 (101.3)		-399.414442 (-5.9)
	RHF/6-31G*	-401.635045 (0)	"cis" -401.531441 (65.0)	"cis" -401.599857 (22.1)	-401.477229 (99.0)		-401.645105 (-6.3)
	Becke3lyp/ 6-31G*	-404.300526 (0)	"cis" -404.230017 (44.2)	"cis" -404.261468 (24.5)	-404.173793 (79.5)		-404.311561 (-6.9)
	MP2/6-311G**// RHF/6-31G*	-403.173123 (0)	"cis" -403.096683 (48.0)	"cis" -403.136241 (23.1)	-403.051643 (76.2)		-403.191292 (-11.4)
	MP2/6-31G*// RHF/3-21G	-402.931429 (0)	"cis" -402.871935 (37.3) "trans" -402.867581 (40.1)	"cis" -402.895964 (22.3) "trans" -402.895593 (22.5)	-402.803297 (80.4)		-402.946163 (-9.2)

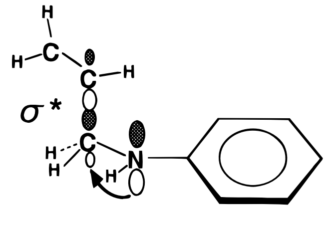
* **B** (intermediate) in Figure 3a

to not seriously impact the **TS1** geometry. Four computational methods give similar **TS1** structures. In Table 1, computed activation and reaction energies are displayed. For reaction 1, MP4/6-31G*//RHF/3-21G (or

Scheme 1



Scheme 2



due to the large charge-donating strength of the nitrogen lone-pair orbital

Scheme 3

ΔH

+ 88 kcal/mol − (+ 176.3 kcal/mol) = - 88.3 kcal/mol

C − O ⟶ C = O

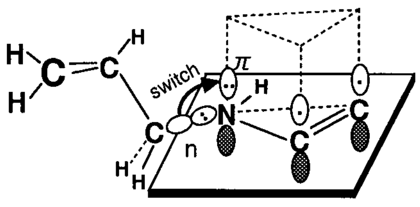
+ 73.2 kcal/mol − (+ 147.0 kcal/mol) = - 73.8 kcal/mol

C − N ⟶ C = N

in **A** (carbon is in the aromatic ring) in **C**

Scheme 4

For **TS1(cis)**



Becke3LYP/6-31G*) activation energy is 26.4 (or 27.4) kcal/mol, which is close to 28.2 kcal/mol[14] and similar to 29.8 kcal/mol[2] and 25.4 kcal/mol.[15] Figure 2 shows geometries of reaction 2. Noteworthy is the result that **TS1(cis)** is 3.1 kcal/mol more favorable than **TS1(trans).** The cis direction of the N−H bond should be related to the reaction course of the rearrangement. Reactions 1 and 2 are compared. The incipient C⋯C bond in **TS1(cis)** of reaction 2 is slightly smaller than that in **TS1** of reaction 1 by four computational methods. The former TS is somewhat later than the latter. In Table 1, the activation energy of reaction 2 is larger than that of reaction 1. The reaction energies (**D** − **A** energy differences) differ to a greater extent.

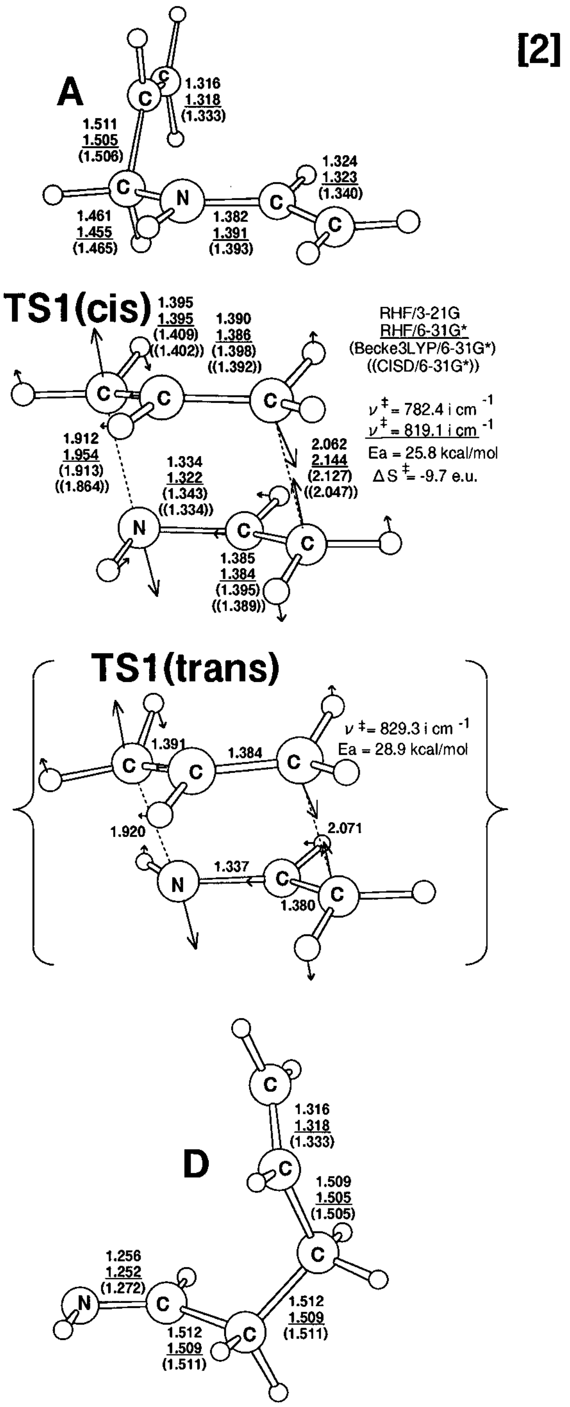


Figure 2. Geometries of reactant **A**, TS, and product (**D**) of reaction 2. The same notations as those in Figure 1 are used.

Figure 3 exhibits geometries of reaction 3. In Figure 3a, the reactant **A** has a geometry wherein the migrating allyl group is separate from the benzene ring. An isomer, **B**, is found. The isomer is only 1.32 kcal/mol less stable than **A**. At an early stage ($s = -5.0$ bohr·amu$^{1/2}$ in Figure 3b), the allyl group is moved toward the reaction center where the C−O bond (=1.484 Å) is not so elongated. The chairlike **TS1** has a geometry quite similar to that of allyl vinyl ether. The cleaving C⋯O bond length of **TS1** is slightly larger in reaction 3 than that in reaction 1. In Table 2, the chairlike **TS1** of reaction 3 is 6.2 kcal/mol more stable than the boatlike TS with MP2/6-31G*//RHF/3-21G. This value is almost the same as 6.6 kcal/mol

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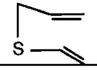
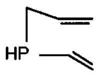
[14] Gajewski, J. J.; Jurayi, J.; Kimbrough, D. R.; Gande, M. E.; Ganem, B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 1170.

[15] Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6983.

Table 3. Total (in au) and Relative (in kcal/mol) Energies of Reactions 5 and 6

Reaction	Methods	**A** (reactant)	**TS1**	**D** (product)
reaction [5] Figure 7 	RHF/3-21G	-588.428747 (0)	-588.382943 (28.7)	-588.435879 (-4.5)
	RHF/6-31G*	-591.454877 (0)	-591.390957 (40.1)	-591.432967 (-13.7)
	Becke3lyp/ 6-31G*	-593.483850 (0)	-593.450737 (20.8)	-593.491370 (-4.7)
reaction [6] Figure 8 	RHF/3-21G	-532.441610 (0)	"cis" -532.388883 (33.1) "trans" -532.383859 (36.2)	-532.434376 (4.5)
	RHF/6-31G*	-535.241704 (0)	"cis" -535.174819 (42.0)	-535.237843 (2.4)
	Becke3lyp/ 6-31G*	-537.242548 (0)	"cis" -537.209368 (20.8)	-537.243506 (-0.6)

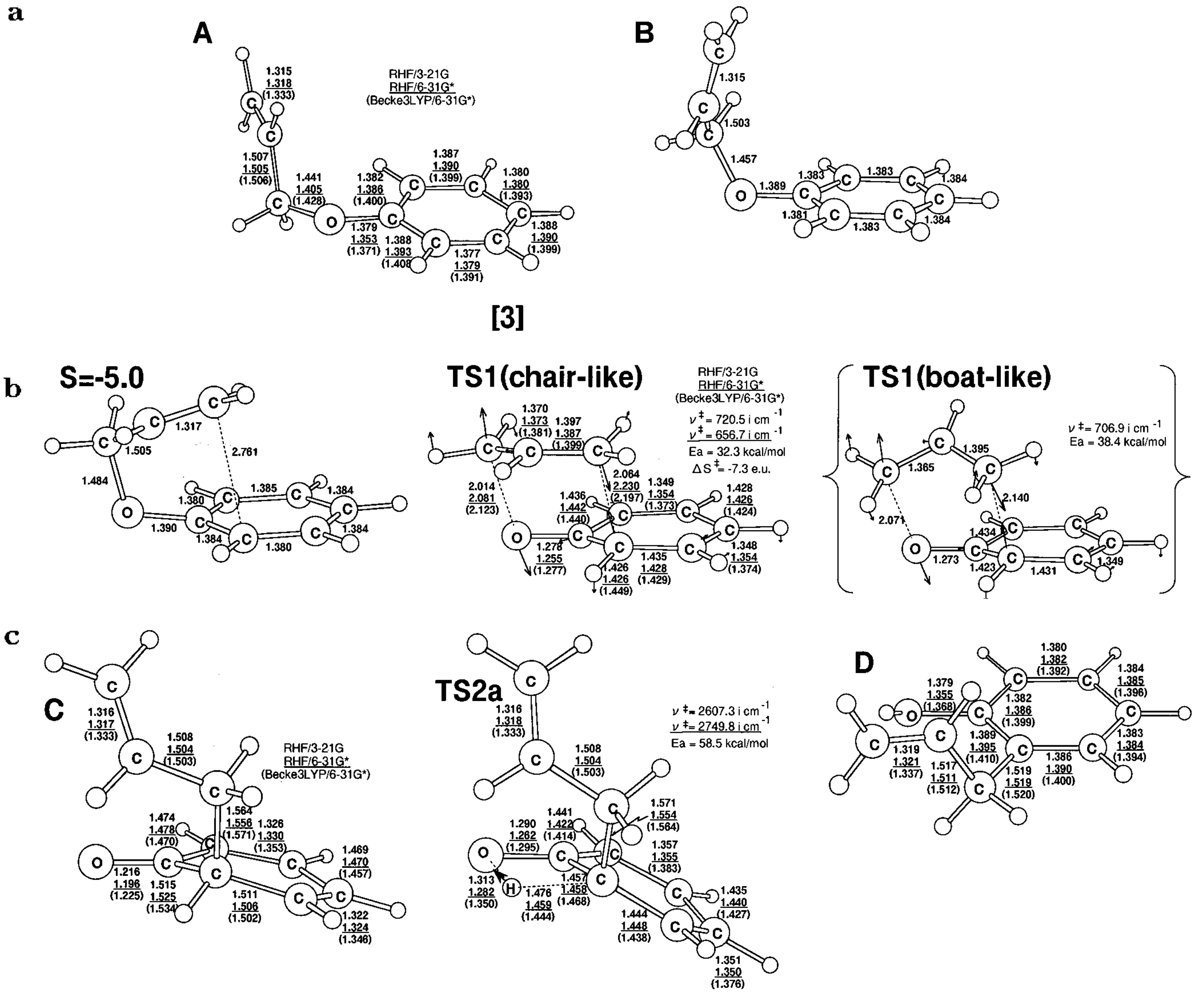


Figure 3. RHF/3-21G geometries of the reactant **A** (allyl phenyl ether), the first intermediate **B**, a point on the intrinsic reaction coordinate ($s = -5.0$ Bohr·amu$^{1/2}$), **TS1**, the second intermediate **C**, **TS2a** (intramolecular hydrogen transfer), and the product **D** (2-allyl phenol) in reaction 3. For two TS structures, **TS1** (chairlike) and **TS2a**, RHF/6-31G* (underlined) and (Becke3LYP/6-31G*) distances are also shown.

obtained in reaction 1. The MP2/6-31G*//RHF/3-21G (or MP2/6-311G**/RHF/6-31G*) activation energy, 32.3 (or 32.6) kcal/mol, is fortunately very close to the experimental one, 32.2 kcal/mol.[16] After **TS1**, an intermediate **C** is formed in Figure 3c. From **C**, a hydrogen atom attached to the ortho carbon atom must move toward the exocylic oxygen atom. For this **C** → **D** isomerization, there are three hydrogen-transfer modes as shown in Scheme 1. Mode c can be ruled out, because Claisen rearrangement occurs under neat conditions. Then, **TS2a** in Figure 3c is compared with **TS2b** in Figure 4. **TS2a** suffers a large 4-membered ring strain. In **TS2b**,

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[16] White, W. N.; Gwynn, D.; Schlitt, R.; Girard, C.; Fife, W. *J. Am. Chem. Soc.* **1958**, *80*, 3271.

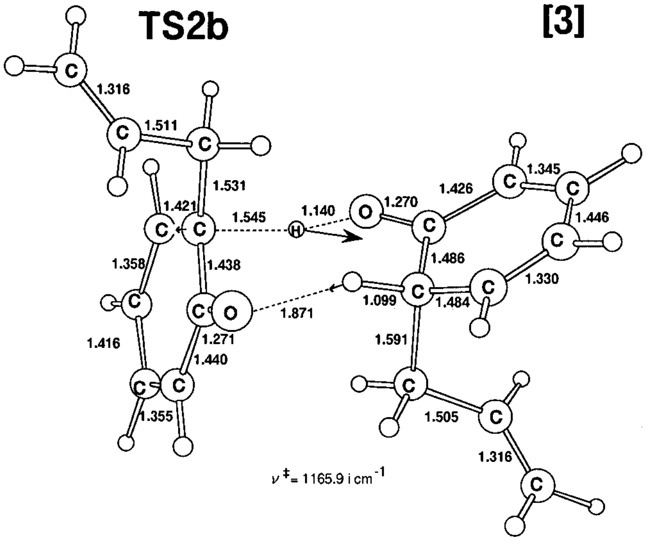

Figure 4. RHF/3-21G TS geometry of an intermolecular double hydrogen transfer between two second intermediates (two **C**'s).

the intermolecular hydrogen transfer is asynchronous. That is, in Figure 4, the upper (rightward) hydrogen migration occurs first, which causes the lower (leftward) migration. In Table 2, **TS2b** is 52.2 kcal/mol (MP2/6-31G*//RHF/3-21G) more stable than **TS2a**. Two hydrogen atoms thus migrate between two intermediates (**C**'s).

Figure 5 shows the geometries of reaction 4. Noticeably, a C−C bond in the allyl group is perpendicular to the aniline plane. The nitrogen lone-pair orbital may donate charge density to the C−C bond (Scheme 2). In fact, the axial C−C length (=1.516 Å) is larger than that (=1.507 Å) in allyl phenyl ether (**A** in Figure 3a). At an early stage (s = −5.0 bohr·amu$^{1/2}$), the chairlike conformation begins to form, which is similar to that in Figure 3b. The **TS1(cis)** geometry in Figure 5a is close to that of **TS1** (chairlike) in Figure 3b. The newly formed C···C distance (1.984 Å) is slightly smaller than that (2.064 Å) in Figure 3b. Apparently, there is no geometric handicap in the **TS1(cis)** of reaction 4. But, in Table 2, E_a = 37.3 kcal/mol (MP2/6-31G*//RHF/3-21G) of reaction 4 is larger than that (32.3 kcal/mol) of reaction 3. The former E_a value is fortuitously in excellent agreement with the experimental one, 37.6 kcal/mol.[9b] More importantly, the **A** → **C** reaction enthalpy (22.3 kcal/mol) of reaction 4 is much larger (more endothermic) than that, 10.0 kcal/mol, of reaction 3. Thus, the contrast between the ready occurrence of reaction 3 and the sluggish occurence of reaction 4 is due to thermodynamic features. Average bond energies and reaction enthalpy differences (Δ*H*'s) are given in Scheme 3. In Scheme 3, the difference in Δ*H* values is −73.8 − (−88.3) = 14.5 kcal/mol. This value is close to that (=22.3−10.0 kcal/mol) between reactions 4 and 3. Indeed the C−O bond in reaction 3 is more difficult to cleave than the C−N bond in reaction 4, but the newly formed C=O bond gains much greater stability than the C=N bond.

In Figure 5b, **TS1(trans)** is shown. The difference between **TS1(trans)** and **TS1(cis)** is only the direction of the N−H bond, as in Figure 2. Shown at the bottom of Table 2, **TS1(cis)** is 2.8 kcal/mol more favorable than **TS1(trans)**. The favorableness of **TS1(cis)** suggests a common feature of all Claisen rearrangements. The first action is the switch of bonding electrons for the allyl group from the in-plane lone-pair electrons to the pπ electrons as in Scheme 4. **A** → **B** in Figure 3 represents the switch. The action carries the allyl group to the broken triangular-prism region in the chair form in Scheme 4.

Figure 6 presents energy diagrams of four Claisen rearrangements. Reaction 1 has the smallest activation

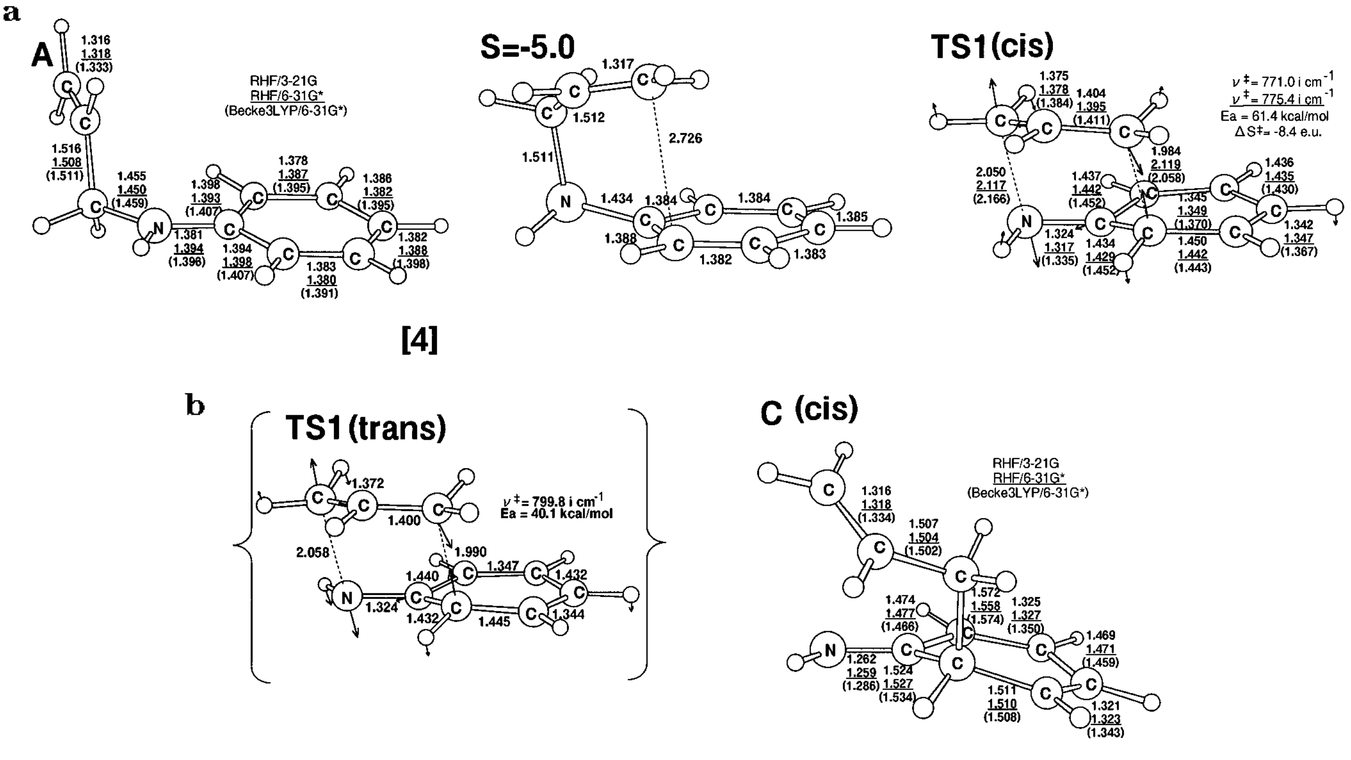

Figure 5. Geometries of the reactant **A** (*N*-allylaniline), a point on the intrinsic reaction coordinate (*s* = −5.0 Bohr·amu$^{1/2}$), **TS1**, and the intermediate **C(cis)** in reaction 4.

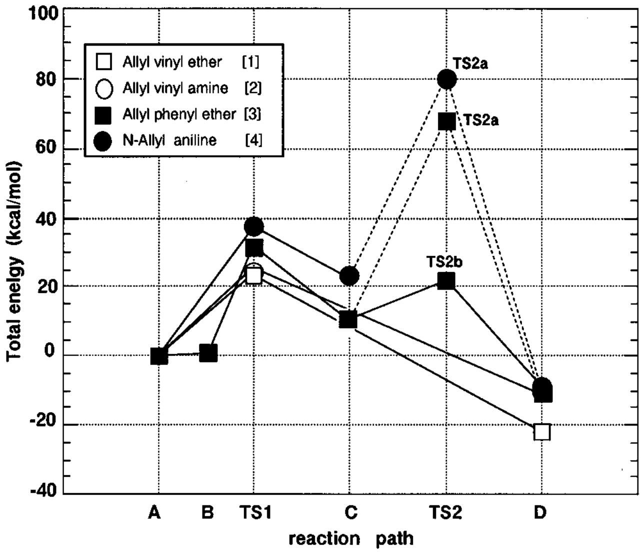

Figure 6. MP2/6-31G*//RHF/3-21G potential energy diagrams of four Claisen rearrangements.

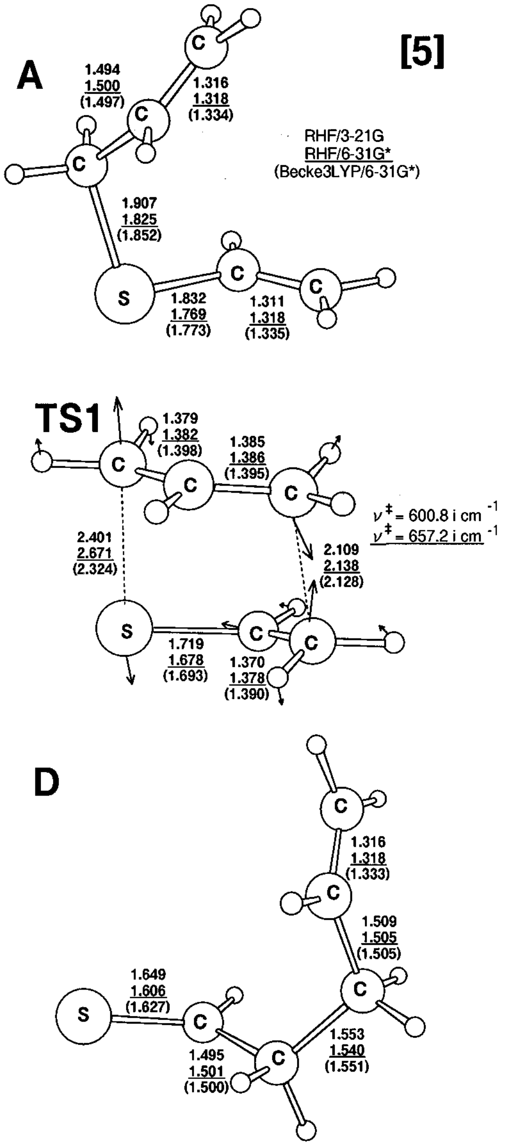

Figure 7. Geometries of reaction 5.

energy. For reaction 3, **TS1** is confirmed to be the rate-determining step.[17] The intermolecular hydrogen transfer (**TS2b**) is much more favorable than the intramolecular one (**TS2a**). While overall exothermic energies (**A** → **D**) of reactions 2–4 are similar, that of reaction 1 is large, −21.4 kcal/mol (Table 1).

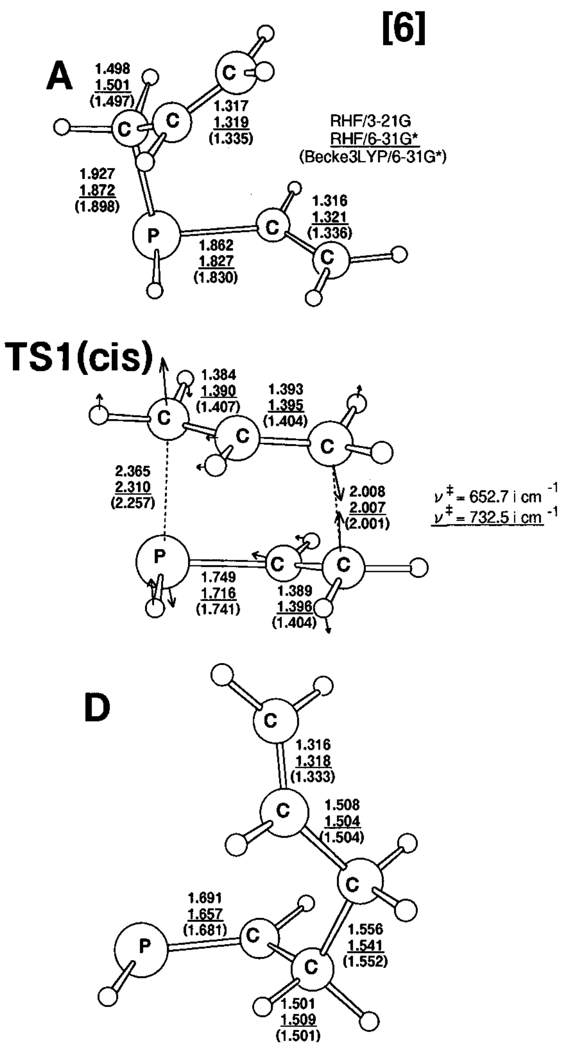

Figure 8. Geometries of reaction 6.

Claisen rearrangements containing the second-row atoms were examined. Figure 7 shows geometries of reaction 5. In general, the sulfur atom has a larger bond distance and a smaller bond angle than the oxygen atom. The sulfur [3,3] shift is expected to proceed more readily than that of oxygen. In fact, geometric changes of reaction 5 along **A** → **TS1** → **D** are smaller than those in reaction 1 in Figure 1. Table 3 shows activation energies of reaction 5. They are similar or smaller than those of reaction 1 in Table 1. However, reaction enthalpies (**D** − **A** energy differences) of reaction 5 are smaller (less exothermic) than those of reaction 1. Thus, the sulfur Claisen shift is more favorable kinetically but less favorable thermodynamically than the oxygen shift. This trend can be recognized when reaction 6 is compared with reaction 2. Figure 8 presents the geometries of reaction 6. This has a smooth geometric change relative to that of reaction 2 in Figure 2. In Tables 1 and 3, reaction 6 is better kinetically but worse thermodynamically than reaction 2. The trend is enhanced in aromatic Claisen rearrangements. Figure 9 shows the geometries of

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[17] Energy diagrams in Figure 6 are shown as differences relative to the total energy of **A**. Total energies of **A**, **TS1**, **C**, and **D** are for a molecule. But, that of **TS2** is for two molecules, half of which is shown in Figure 6.

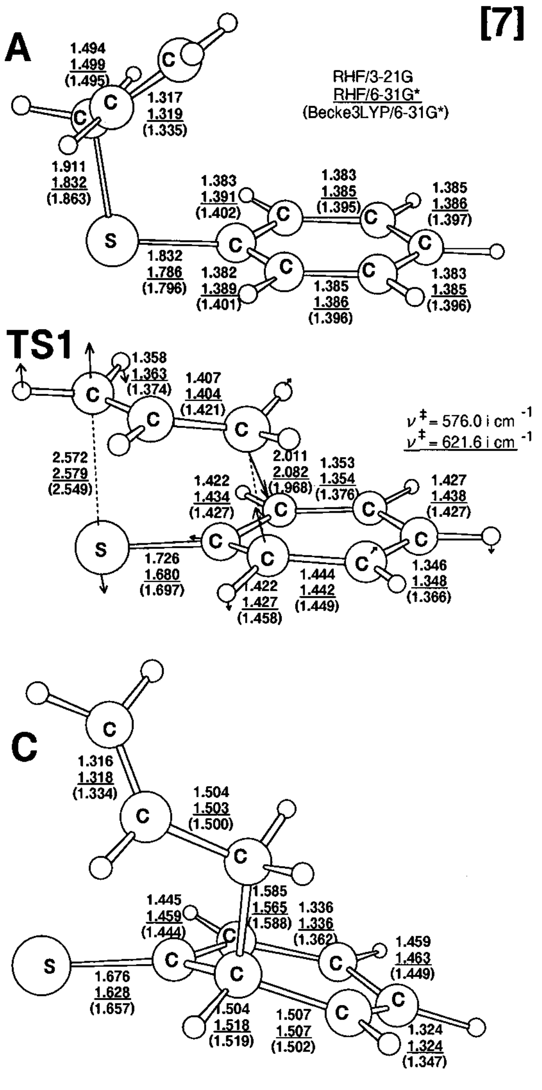


Figure 9. Geometries of reaction 7.

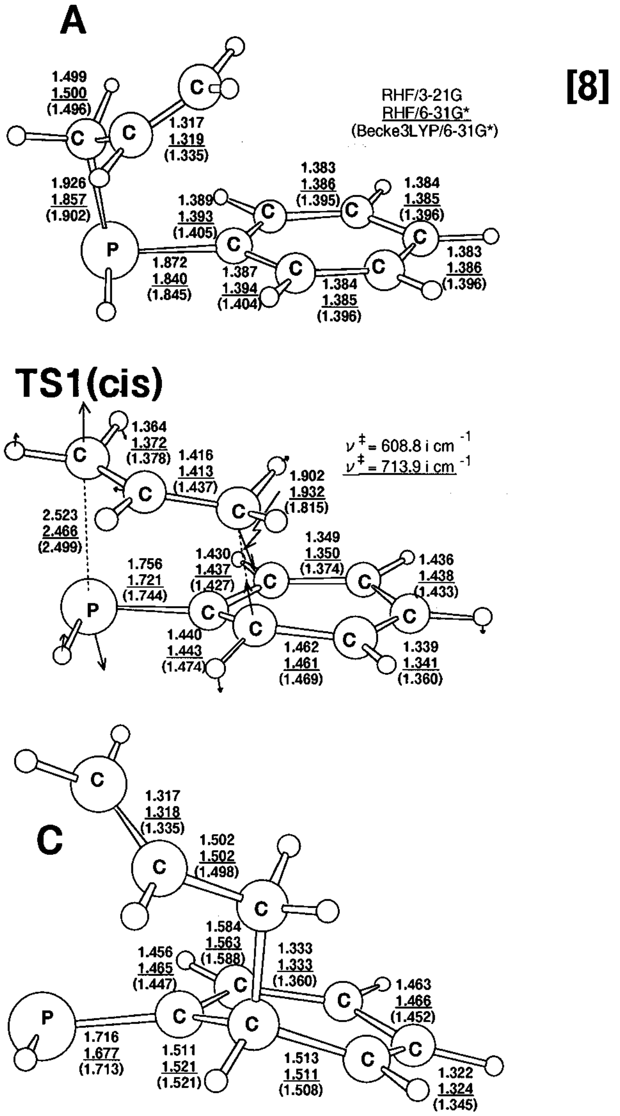


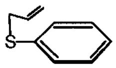
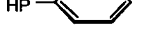
Figure 10. Geometries of reaction 8.

reaction 7. Only a small distortion leads to the **A** → **C** process. However, Table 4 indicates that the process is very endothermic. Figure 10 exhibits geometries of reaction 8. There are only slight geometric changes. But, unfortunately, reaction 8 is the most endothermic of the eight reactions. Aromatic Claisen rearrangements containing the second-row atoms are improbable.

IV. Concluding Remarks

This work has dealt theoretically with aromatic Claisen rearrangements, reactions 3, 4, 7, and 8. Allyl reactions, reactions 1, 2, 5, and 6, have also been investigated for comparison. Ether reactions are found to be more favorable than amine reactions, both kinetically and thermodynamically. In particular, the conversion of C−O → C=O gives rise to great stabilization. Boat-type and cis transition states originate from a switch of the allyl−heteroatom bond positions (Scheme 4). In the second step of reaction 3, two hydrogen atoms are transferred mutually between two intermediates, **C**'s. Claisen rearrangements containing the second-row atoms (reactions 5−8)

Table 4. Total (in au) and Relative (in kcal/mol) Energies of Reactions 7 and 8

Reaction	Methods	**A** (reactant)	**TS1**	**C** (intermediate)
reaction [7] Figure 9 	RHF/3-21G	-740.249515 (0)	-740.182477 (42.1)	-740.208365 (25.8)
	RHF/6-31G*	-744.123148 (0)	-744.039015 (52.8)	-744.081702 (26.0)
	Becke3lyp/ 6-31G*	-747.141115 (0)	-747.088878 (32.8)	-747.103981 (23.3)
reaction [8] Figure 10 	RHF/3-21G	-684.260796 (0)	"cis" -684.179925 (50.8) "trans" -684.175918 (53.3)	-684.200983 (37.5)
	RHF/6-31G*	-687.910464 (0)	"cis" -687.815660 (59.5)	-687.851888 (36.8)
	Becke3lyp/ 6-31G*	-690.901579 (0)	"cis" -690.841929 (37.4)	-690.851039 (31.7)

are more favorable kinetically but less favorable thermodynamically than those containing the first-row atoms (reactions 1−4). As a reaction design, the oxygen atom is the best atom for Claisen rearrangements. This is because C−O and C=O bond energies are extraordinarily different.

Supporting Information Available: Cartesian coordinates (39 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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