

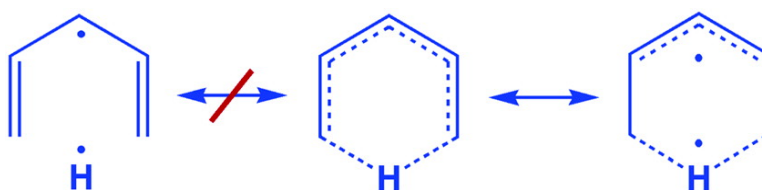
Article

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## A B3LYP Study of the Effects of Phenyl Substituents on 1,5-Hydrogen Shifts in 3-(Z)-1,3-Pentadiene Provides Evidence Against a Chameleonic Transition Structure

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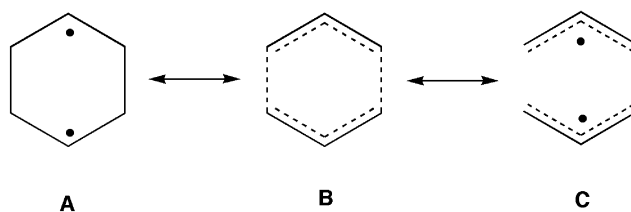
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**Abstract:** The effects of one or two phenyl substituents on the activation enthalpy for a 1,5-hydrogen shift in 3-(Z)-1,3-pentadiene (**1**) and on the geometry of the transition structure (TS) have been investigated by B3LYP/6-31G\* calculations. The phenyl-substituent effects on the experimentally measured activation enthalpies are predicted to be sizable, spanning a range of nearly 10 kcal/mol. However, if differences between steric effects in the transoid isomers of the reactants are factored out by comparing the activation enthalpies in the cisoid conformers, the electronic components of the phenyl-substituent effects on both the barrier heights and the TS geometries are found to be quite modest in size. Unlike the TS in the Cope rearrangement, the TS for a 1,5-hydrogen shift in **1** is not highly variable in nature, and the reason the 1,5-hydrogen shift TS is not chameleonic is discussed.

The nature of the transition structure (TS) for the Cope rearrangement of 1,5-hexadiene has been the subject of a great deal of experimental and computational research.<sup>1</sup> Pioneering studies by Gajewski and Conrad found that H/D secondary kinetic isotope effects (KIES) on the rate of this reaction depend on the number and placement of radical stabilizing substituents.<sup>2</sup> This finding was interpreted by the authors as being indicative of a variable TS for the Cope rearrangement, the structure of which could be altered by substituents.

For example, the KIEs found by Gajewski and Conrad for phenyl substituents at C2 and C5 suggested a TS resembling cyclohexane-1,4-diyl (structure **A** in Figure 1). In contrast, the KIEs measured for a pair of cyano substituents at C3 indicated that the TS had changed toward one that could better be described as consisting of two weakly interacting allyl radicals (structure **C** in Figure 1).

The measured effects of multiple phenyl substituents on the rate of Cope rearrangement of 1,5-hexadienes<sup>3</sup> were also shown to be consistent with variable or “chameleonic” Cope TSs.<sup>4</sup> In 1,5-hexadienes, in which the positions of all of the phenyl substituents favor a TS with either short or long interallylic C–C bonds, cooperative substituent effects were observed.<sup>3a–c,f</sup> In contrast, with phenyl or cyano substituents at C1 and C3, the effect of a phenyl substituent at C5 on the rate was found to be



**Figure 1.** Possible contributors to the TSs for Cope rearrangements of 1,5-hexadienes.

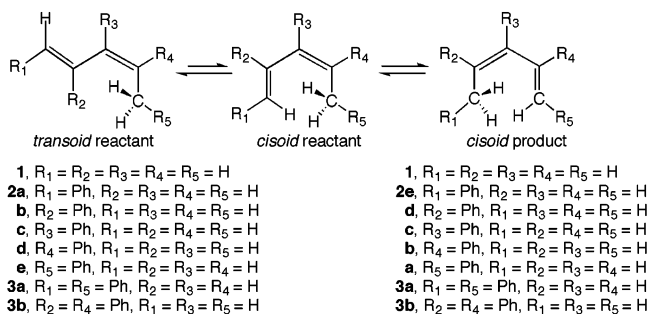
competitive, rather than cooperative.<sup>3d,e</sup> B3LYP/6-31G\* calculations reproduced the experimental activation enthalpies very well, and the TS geometries showed that the competitive and cooperative substituent effects were, in fact, due to substituent-induced changes of the bond lengths in the TS.<sup>4</sup>

Do other Woodward–Hoffmann allowed pericyclic reactions<sup>5</sup> have a similar variability in rate and TS geometry, so that they exhibit chameleonic behavior upon the placement of phenyl substituents at different carbons? To address this question for a different type of sigmatropic reaction, we have carried out

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(1) Reviews: (a) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 166–176. (b) Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213. (c) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (d) Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81. (e) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67. (f) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378. (2) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693.

(3) (a) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 4417. (b) Roth, W. R.; Lennartz, H.-W.; Doering, W. von E.; Birladeanu, L.; Guyton, C. A.; Kitagawa, T. *J. Am. Chem. Soc.* **1990**, *112*, 1722. (c) Doering, W. von E.; Birladeanu, L.; Sarma, K.; Teles, J. H.; Klärner, F.-G.; Gehrke, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 4289. (d) Doering, W. von E.; Wang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10112. (e) Doering, W. von E.; Wang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10967. (f) Doering, W. von E.; Birladeanu, L.; Sarma, K.; Blaschke, G.; Scheidmantel, U.; Boese, R.; Benet-Buchholz, J.; Klärner, F.-G.; Gehrke, J.-S.; Zinny, B. U.; Sustmann, R.; Korth, H.-G. *J. Am. Chem. Soc.* **2000**, *122*, 193. (4) (a) Hrovat, D. A.; Chen, J.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 7456. For other computational studies of the effects of substituents on Cope rearrangements, see: (b) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, Y.-H.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 10529. (c) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 7456. (5) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.



**Figure 2.** 3-(Z)-1,3-Pentadienes on which calculations were performed in this study.

calculations on the 1,5-hydrogen shift in (Z)-1,3-pentadiene (**1**)<sup>6</sup> and in phenyl-substituted derivatives **2** and **3** (Figure 2). Two recent computational papers have dealt with the effects of different types of substituents on the rate of 1,5-hydrogen shifts,<sup>7,8</sup> but neither of these investigations addressed the question of whether the TS for this reaction is chameleonic. Herein, we report the results of our study, which was focused on this issue.

### Computational Methodology

B3LYP/6-31G\* calculations gave excellent agreement with experiment in our studies of phenyl-substituent effects on the Cope rearrangement,<sup>4a</sup> and this level of theory also has been found to provide a calculated enthalpy of activation for the 1,5-hydrogen shift in unsubstituted 3-(Z)-1,3-pentadiene (**1**)<sup>7a,9–11</sup> that is in excellent agreement with the experimental values, measured by Roth<sup>12</sup> and by Frey.<sup>13</sup> Therefore, our calculations of the substituent effects on the 1,5-hydrogen shifts in phenyl-substituted 3-(Z)-1,3-pentadienes were carried out with the three-parameter functional of Becke,<sup>14</sup> the correlation functional of Lee, Yang, and Parr,<sup>15</sup> and the 6-31G\* basis set.<sup>16,17</sup>

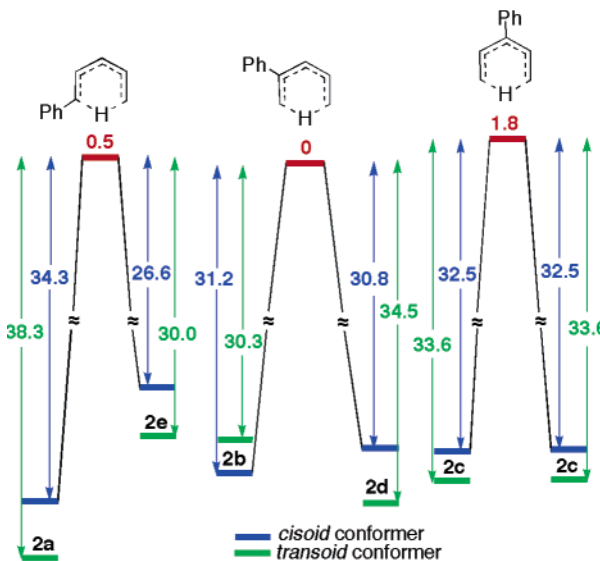
Geometries were optimized and vibrational analyses were performed at the B3LYP/6-31G\* level of theory. The vibrational analyses were used to characterize each stationary point as an energy minimum or TS; and the harmonic frequencies from the vibrational analyses were used, without scaling, to compute zero-point energies. All of the calculations were carried out with the Gaussian 98 suite of programs.<sup>18</sup>

- (6) For a brief review and leading references, see: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 106–107.
- (7) (a) Saettel, N. J.; Wiest, O. *J. Org. Chem.* **2000**, *65*, 2331. (b) Alabugin, I. V.; Manoharan, M.; Breiner, B.; Lewis, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 9329.
- (8) For a B3LYP study of 1,5-hydrogen shifts in cyclic dienes, see: Hess, B. A., Jr.; Baldwin, J. E. *J. Org. Chem.* **2002**, *67*, 6025.
- (9) (a) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1988**, 2497. (b) Jursic, B. *J. Mol. Struct. (THEOCHEM)* **1988**, *423*, 189.
- (10) The results of high quality ab initio calculations on this reaction also provide activation enthalpies that agree well with experiment. Jiao, H.; Schleyer, P. von R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1559.
- (11) Semiempirical calculations have found that tunneling has a significant effect on the activation parameters for this reaction. Liu, Y.-P.; Lynch, G. C.; Truong, T. N.; Lu, D.-H.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *115*, 2408. Either the agreement of the B3LYP<sup>7a,9</sup> and ab initio<sup>10</sup> activation enthalpies, which did not include tunneling corrections, with the experimental values is fortuitous, or tunneling has a much smaller effect on the activation enthalpies than is indicated by these semiempirical calculations, which did include tunneling corrections.
- (12) Roth, W. R.; König, J. *Justus Liebig's Ann. Chem.* **1966**, *699*, 24.
- (13) (a) Frey, H. M.; Ellis, R. J. *J. Chem. Soc. A* **1965**, 4770. (b) Frey, H. M.; Pope, B. M. *J. Chem. Soc. A* **1966**, 1701.
- (14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (15) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.
- (16) Harihan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- (17) Inclusion of the polarization functions on hydrogen in the 6-31G\*\* basis set was found to have only a small effect on the computed enthalpy of activation for a degenerate 1,5-hydrogen shift in **1**, lowering the calculated value by just 0.6 kcal/mol.

**Table 1.** B3LYP/6-31G\* Enthalpies of Activation (kcal/mol) for 1,5-Hydrogen Shifts in the Cisoid and Transoid Conformations of 3-(Z)-1,3-Pentadiene (**1**), Five Monophenyl Derivatives (**2a–e**), and Two Diphenyl Derivatives (**3a** and **b**)<sup>a</sup>

diene	$\Delta H_{\text{transoid}}^\ddagger$	$\Delta H_{\text{cisoid}}^\ddagger$	$\Delta H_{\text{rel}} \text{ TS}$
<b>1</b>	35.6	32.0	
<b>2a</b>	38.3	34.3	0.5
<b>2b</b>	30.3	31.2	0
<b>2c</b>	33.6	32.5	1.8
<b>2d</b>	34.5	30.8	0
<b>2e</b>	30.0	26.6	0.5
<b>3a</b>	32.6	28.8	0.6
<b>3b</b>	28.8	29.9	0

<sup>a</sup> Relative enthalpies (kcal/mol) of isomeric transition structures (TSs) are also given.

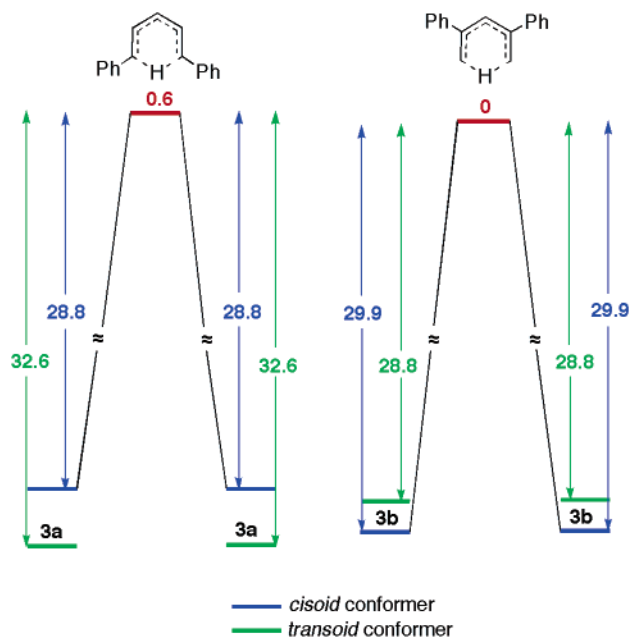


**Figure 3.** B3LYP/6-31G\* enthalpies of activation (kcal/mol) for 1,5-hydrogen shifts in the cisoid and transoid conformations of phenyl-substituted 3-(Z)-1,3-pentadienes **2a–e**. Relative enthalpies of the TSs for these reactions are given in red.

### Results

The results of our calculations on 1,5-hydrogen shifts in 3-(Z)-1,3-pentadiene (**1**), in five of the six possible monophenyl derivatives (**2a–e**), and in two diphenyl derivatives (**3a** and **b**), are summarized in Table 1<sup>19</sup> and displayed graphically in Figures 3 and 4. Calculations were not performed on 1-phenyl-trans-1-(Z)-3-(Z)-1,3-pentadiene, because in this stereoisomer the C1 phenyl group makes a cisoid conformation about the bond between C2 and C3 prohibitively high in energy. As illustrated in Figure 2, a cisoid conformation about this bond is necessary for a 1,5-hydrogen atom shift from C5 to C1 in **1–3**.

- (18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (19) Optimized geometries and electronic energies of reactants and TSs are available as Supporting Information.



**Figure 4.** B3LYP/6-31G\* enthalpies of activation (kcal/mol) for 1,5-hydrogen shifts in the cisoid and transoid conformations of phenyl-substituted 3-(Z)-1,3-pentadienes **3a** and **b**. Relative enthalpies of the TSs for these reactions are given in red.

**Enthalpy Differences between the Reactants.** Because **2a** and **2e** are connected by the same transition structure (TS), the calculated difference of 8.3 kcal/mol in their enthalpies of activation for 1,5-hydrogen shift is equal to the enthalpy difference between these two constitutional isomers.<sup>20</sup> This large calculated difference in relative thermochemical stabilities is due to the fact that the phenyl group is conjugated with a double bond in **2a** but not in **2e**.

We have previously noted that B3LYP/6-31G\* calculations overestimate by several kcal/mol the enthalpic preference for conjugated, versus nonconjugated phenyl groups.<sup>4</sup> Nevertheless, the prediction that the rearrangement of **2e** to **2a** ( $\Delta H = -8.3$  kcal/mol) should be more exothermic than the rearrangement of **2b** to **2d** ( $\Delta H = -3.3$  kcal/mol) is almost certainly correct.

**2b** and **2d** are also connected by a common transition structure. Therefore, as in the case of **2a/2e**, the calculated difference between the enthalpies of activation for 1,5-hydrogen shift in **2b** and **2d** is equal to the enthalpy difference between these two constitutional isomers. However, unlike the case in **2a/2e**, the 3.3 kcal/mol higher enthalpy of **2b**, relative to **2d**, is largely steric, rather than electronic, in origin.

A transoid conformation about the single bond between C2 and C3 places the phenyl group at C2 in **2b** in a syn relationship to the methyl group at C4. The steric interaction between these two groups is so severe that in **2b**, unlike the case in any of the other four constitutional isomers of **2**, the cisoid conformation is actually predicted to be preferred to the transoid, albeit by only 0.9 kcal/mol.

In contrast to the case in **2b**, in **2d** the conformation about the single bond between C2 and C3 has almost no effect on the

steric interactions involving the phenyl group at C4. In **2d** a transoid conformation about this single bond is predicted to be preferred to a cisoid conformation by 3.7 kcal/mol, which is essentially the same enthalpy difference that is computed between these two conformations in unsubstituted 1,5-pentadiene. Thus, there is a change of  $3.7 - (-0.9) = 4.6$  kcal/mol in the relative enthalpies of the cisoid and transoid conformations between **2d** and **2b**.

The transoid conformation of **2c** also suffers some steric destabilization, in this case due to the phenyl group at C3 interacting with the syn hydrogen at C1. As a consequence, the enthalpy difference of 1.1 kcal/mol between cisoid and transoid conformations in **2c** is smaller than that (3.7 kcal/mol) in **2d**, but not as small as that ( $-0.9$  kcal/mol) in **2b**. The enthalpy differences of 4.0 and 3.4 kcal/mol between the cisoid and transoid conformations of, respectively, **2a** and **2e** are close to the enthalpy difference between these two conformations of **2d**.

Except for diene **2b**, which is calculated to prefer a cisoid conformation, the activation enthalpies in Table 1 for the transoid conformers of **2a**, **2c**, **2d**, and **2e** are those predicted to be measured experimentally.<sup>21</sup> However, these enthalpies of activation each contain a contribution from the enthalpy difference between the preferred transoid conformation of the reactant and the necessarily cisoid conformation of the TS. As noted above, these contributions are different for the different constitutional isomers of **2**.

**Activation Enthalpies for the Cisoid Conformers.** To assess the purely electronic effects of the phenyl substituents in **2a–e** on the activation enthalpies for the 1,5-hydrogen shifts in these five 3-(Z)-1,3-pentadienes, it is necessary to factor out the contributions from differences between steric effects in the reactants and TSs. Toward this end, in Table 1 and Figure 3 we also compare the calculated enthalpies of activation for 1,5-hydrogen shifts, starting with the cisoid conformers of **2a–e**. The differences between the activation enthalpies for a 1,5-hydrogen shift in the cisoid and transoid conformations of **2a–e** are, of course, equal to the enthalpy difference between these two conformers in each of the five dienes.

Table 1 shows that the 1,5-hydrogen shifts in transoid **2b** and **2c** are predicted to occur with activation enthalpies that are, respectively, 5.3 and 2.0 kcal/mol lower than that in transoid **1**. However, in the cisoid conformers of **2b** and **2c**, where the steric interactions that destabilize the transoid conformers are absent, the enthalpies of activation for the 1,5-hydrogen shifts are computed to be, respectively, 0.8 kcal/mol lower and 0.5 kcal/mol higher than in cisoid **1**. Thus, the phenyl substituent at C2 in **2b** and at C3 in **2c** is predicted to have little electronic effect on lowering the activation enthalpies for 1,5-hydrogen shift in the cisoid conformers from the value of  $\Delta H^\ddagger = 32.0$  kcal/mol calculated for the cisoid conformer of **1**. Therefore, the effect of the phenyl substituents on making the calculated activation enthalpies for a 1,5-hydrogen shift in the transoid conformers of **2b** and **2c** lower than the activation enthalpy in the transoid conformer of **1** is largely steric in nature.

In contrast to the case in **2b** and **2c**, the steric environment of the phenyl group is similar in both cisoid and transoid

(20) The amount of **2e** formed by equilibrating **2a** with **2e** is expected to be too small to allow an accurate determination of the enthalpy of activation for the 1,5-hydrogen shift that isomerizes **2a** to **2e**. However, starting with **2a-1-d<sub>1</sub>**, the temperature dependence of the rate of formation of **2a-5-d<sub>1</sub>** should allow the experimental determination of this activation enthalpy. Measurement of the activation enthalpy for the rearrangement of **2e** to **2a** would then provide the enthalpy difference between these two isomers.

(21) In **2b** and **2c**, the cisoid and transoid conformations are both expected to be appreciably populated at the temperatures necessary for convenient rate studies; so the measured enthalpy of activation should actually be a population-weighted average of the enthalpies of activation for each of these conformers.



conformations of **2a**, **2d**, and **2e**. It is for this reason that the differences in the enthalpies of activation for 1,5-hydrogen shifts between these three phenyl-substituted 1,3-pentadienes and **1** are calculated to be about the same in the cisoid as in the transoid conformers.

As Table 1 shows, the activation enthalpies for 1,5-hydrogen shift in the cisoid conformers of **2b** and **2d** are both ca. 1 kcal/mol lower than that in cisoid **1**, but the activation enthalpy in the cisoid conformer of **2c** is actually 0.5 kcal/mol higher than that in cisoid **1**. Obviously, placement of a phenyl group at C2 or C4 of **1** does result in at least a small amount of selective stabilization of the TS, relative to the reactant, whereas phenyl substitution at C3 has the opposite effect.

The high exothermicity of the rearrangement of **2e** to **2a** makes comparison of the activation enthalpy for either the forward or the backward reaction with that for the degenerate rearrangement of **1** meaningless. However, Marcus theory shows that the intrinsic barrier to the 1,5-hydrogen shift that equilibrates **2a** and **2e** is approximately equal to the average of the activation enthalpies for the forward and backward reactions.<sup>22</sup>

If the average of the activation enthalpies for the reactions that equilibrate the cisoid conformations of **2a** and **2e** (30.5 kcal/mol) is compared with  $\Delta H^\ddagger = 32.0$  kcal/mol for a 1,5-hydrogen shift in cisoid **1**, the presence of a phenyl substituent at a terminal carbon appears to reduce the intrinsic barrier to reaction by 1.5 kcal/mol. This reduction in barrier height is 0.5 kcal/mol larger in size than the reduction of 1.0 kcal/mol caused by a phenyl substituent at C2(C4).

Because the three TSs in Figure 3 are isomers, it is possible to address the question of how the position of the phenyl group affects the enthalpy of just the TS for a 1,5-hydrogen shift. The TS of lowest enthalpy is that for the equilibration of **2b** and **2d**, in which the phenyl substituent is at C2(C4). The TS for the rearrangement of **2e** to **2a**, which has the phenyl substituent at C1(C5), is higher in enthalpy by 0.5 kcal/mol, and the TS for the degenerate rearrangement of **2c** is 1.3 kcal/mol higher still.

Although a phenyl group at C2(C4) is 0.5 kcal/mol more effective in lowering the enthalpy of the TS than a phenyl group at C1(C5), it is 0.5 kcal/mol less effective in lowering the intrinsic barrier to a 1,5-hydrogen shift in the cisoid conformer of **1**. It then follows that the average enthalpy of the cisoid conformers must be 1.0 kcal/mol higher in **2a** and **2e** than in **2b** and **2d**. This fact, which can be easily verified from the enthalpies given in Table 1 or in Figure 3, is due to the phenyl group in **2e** not being attached to a doubly bonded carbon.

However, whether the activation enthalpies for 1,5-hydrogen shifts in the cisoid conformers are compared, or whether a comparison is made between the enthalpies of just the TSs for these reactions, it is clear that a phenyl group at C1/C5 or C2/C4 is 1–2 kcal/mol more effective than a phenyl group at C3 at stabilizing the TS for a 1,5-hydrogen shift in 3-(Z)-1,3-pentadiene.

**Effects of Multiple Phenyl Substituents.** Table 1 and Figure 4 show the effects of the pair of phenyl substituents at C1 and C5 in **3a** and at C2 and C4 in **3b** on the activation enthalpy for

a 1,5-hydrogen shift. As is the case with the monophenyl-substituted dienes (**2a–e**), the results for the cisoid conformers are more informative about the electronic effects of the phenyl substituents in **3a** and **3b** than the results for the transoid conformers.

The rearrangements of **3a** and **3b** are, like the rearrangements of **1** and **2c**, degenerate. As already noted, the phenyl substituent at C3 in cisoid **2c** actually increases the activation enthalpy by 0.5 kcal/mol over that for the 1,5-hydrogen shift in cisoid **1**. In contrast, the phenyl groups at C1 and C5 in cisoid **3a** lower the activation enthalpy by 1.6 kcal/mol per phenyl group, relative to that in cisoid **1**, and the phenyl groups at C2 and C4 in cisoid **3b** lower the activation enthalpy by 1.1 kcal/mol per phenyl group, relative to that in cisoid **1**.

Although the phenyl groups at C1 and C5 in cisoid **3a** have a larger effect than the phenyl groups at C2 and C4 in cisoid **3b** on lowering the energy of the TS, relative to the reactants, the TS for rearrangement of cisoid **3b** is 0.6 kcal/mol lower in energy than the TS for rearrangement of cisoid **3a**. The reason is again that one of the phenyl groups in **3a** is not conjugated with a double bond. Consequently, cisoid **3a** is 1.6 kcal/mol higher in energy than cisoid **3b**.

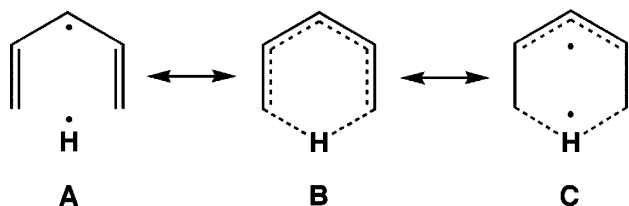
The effects of the pair of phenyl substituents in **3a** and **3b** on lowering the activation enthalpy for a 1,5-hydrogen shift in cisoid **1** are much smaller than those of the pair of phenyl substituents in 2,5-diphenyl-1,5-hexadiene on lowering the activation enthalpy for the Cope rearrangement of 1,5-hexadiene. The pair of phenyl substituents in cisoid **3a**, which give a 1.1 kcal/mol larger substituent effect than the pair in cisoid **3b**, lower the activation enthalpy from that for a 1,5-hydrogen shift in cisoid **1** by 3.2 kcal/mol. For comparison, a pair of phenyl groups at C2 and C5 lower the activation enthalpy for the Cope rearrangement of 1,5-hexadiene by 12 kcal/mol.<sup>3a,b</sup>

Another difference between the phenyl-substituent effects on the two rearrangements is that those for the rearrangement of cisoid **1** appear to be roughly additive, whereas those on the Cope rearrangement are cooperative.<sup>4</sup> For example, as discussed above, the effect of a single phenyl substituent on the interconversions of cisoid **2a/2e** and **2b/2d** amounts to a lowering of the activation enthalpy for rearrangement of cisoid **1** by, respectively, ca. 1.5 and 1.0 kcal/mol. The pair of phenyl substituents in cisoid **3a** and **3b** lowers the activation enthalpy for rearrangement of cisoid **1** by, respectively, 3.2 and 2.1 kcal/mol.

In contrast, a pair of phenyl substituents at C2 and C5 of 1,5-hexadiene lower the activation enthalpy for Cope rearrangement by 3 times as much as a single phenyl substituent.<sup>3a,b</sup> Similarly, phenyl substituents at C1, C3, C4, and C6 of 1,5-hexadiene<sup>1f</sup> lower the activation enthalpy for Cope rearrangement by 3–4 times as much as a pair of phenyl substituents at C1 and C3<sup>1d</sup> or C1 and C4.<sup>1c</sup> As noted in the Introduction, these cooperative substituent effects provide evidence for a variable TS in the Cope rearrangement, that is, a TS whose geometry changes with the number of phenyl substituents and the carbons to which they are attached.<sup>4</sup>

**Effects of Phenyl Substituents on the Geometry of the TS for the Rearrangement of 1.** The best evidence that the cooperative phenyl-substituent effects, seen in the Cope rearrangement of 1,5-hexadienes, are due to a variable TS for this reaction comes from calculations which find that the TS

(22) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) The Marcus equation actually predicts that the average activation enthalpy should be greater than the intrinsic barrier by the square of the exothermicity, divided by 16 times the intrinsic barrier. However, this quotient amounts to only about 0.1 kcal/mol.



**Figure 5.** Possible contributors to the TS for 1,5-hydrogen shift in **1** and derivatives.

**Table 2.** B3LYP/6-31G\* Bond Lengths (Å) in the Transition Structures (TSs) for the Degenerate Rearrangements of Dienes **1**, **2c**, **3a**, and **3b** by 1,5-Hydrogen Shifts<sup>a</sup>

TS for diene	C1–H	C1–C2	C2–C3	Cn–Ph
<b>1</b>	1.427	1.418	1.397	
<b>2c</b> <sup>c</sup>	1.429	1.416	1.404	1.491
<b>3a</b> <sup>d</sup>	1.430	1.429	1.395	1.486
<b>3b</b> <sup>d</sup>	1.411	1.431	1.406	1.486
pentadienyl•		1.364	1.424	

<sup>a</sup> For comparison, the UB3LYP/6-31G\* C–C bond lengths in the planar, all-*cis* geometry of pentadienyl radical<sup>b</sup> are also given. <sup>b</sup> The *C*<sub>2</sub> equilibrium geometry of pentadienyl radical has a C1–C2–C3–C4 dihedral angle of 13.6°, essentially the same C–C bond lengths, and is only 0.4 kcal higher in energy than the *C*<sub>2v</sub> geometry. <sup>c</sup> Because the phenyl group is rotated out of the plane of C2–C3–C4, this TS does not have an element of symmetry. The C5–H bond length is 0.012 Å shorter than the C1–H bond length, given in the table. The C4–C5 and C1–C2 bond lengths are the same, but the C3–C4 bond length is 0.003 Å longer than the C2–C3 bond length. <sup>d</sup> As in the TS for **2c**, the phenyl groups in the TSs for **3a** and **3b** are also partially rotated out of conjugation with the 2p- $\pi$  orbitals on the carbons to which they are attached.

geometry depends strongly on the substitution pattern.<sup>4a</sup> The ability of substituents to alter the TS geometry has been attributed to the ability of either of the diradical resonance structures in Figure 1 to contribute to the Cope TS. The chameleonic nature of the Cope TS means that only small amounts of energy are required for shortening or lengthening the interallylic bonds in the TS.<sup>4</sup>

It is easy to see how the diradical in structure **A** of Figure 5, which resembles pentadienyl radical plus a hydrogen atom, might contribute to the TS for 1,5-hydrogen shift in cisoid **1**, but, at least initially, it is harder to understand why the diradical in structure **C**, which resembles an allylic radical plus a hydrogen atom bonded to the two remaining carbons, would make an appreciable contribution. If only one of the two diradical structures in Figure 5 contributes to the TS for rearrangement of cisoid **1**, one might expect that the geometry of the TS would be much less variable than that for the Cope rearrangement.

The finding that the phenyl-substituent effects on the enthalpy of activation for the rearrangement of cisoid **1** are small and additive, rather than large and cooperative, suggests that the TS for a 1,5-hydrogen shift is not chameleonic. However, the best test of whether the geometry of the TS changes significantly with phenyl substitution is obviously to compare the bond lengths in the TS for the rearrangement of **1** with those for the rearrangements of **2c**, **3a**, and **3b**. All four of these rearrangements are degenerate, and the TSs for them either have or (in the case of the TS for rearrangement of **2c**) almost have a plane of symmetry, which makes comparison of the TS geometries appropriate.

Shown in Table 2 are the C–C and the C–H bond lengths in these four TSs. The largest changes in C–C bond lengths, predicted to be caused by two phenyl groups, are the increases

of 0.013 Å in C1–C2 and 0.009 Å in C2–C3 in the TS for rearrangement of **3b**, relative to these C–C bond lengths in the TS for rearrangement of **1**. For comparison, in the Cope rearrangement of 1,5-hexadiene a pair of phenyl groups at C1 and C4 lengthen the interallylic C–C bonds in the TS by 0.276 Å and a pair of phenyls at C2 and C5 shorten these bonds by 0.389 Å, relative to those in the TS for unsubstituted **1**.<sup>4a</sup> The changes in C–C bond lengths, caused by the pair of phenyl substituents in the TS for 1,5-hydrogen shift in **3b**, are 20–30 times smaller than the changes in the interallylic C–C bond lengths in the Cope TS, caused by a pair of phenyl substituents.

The bond lengths in the TSs for the degenerate 1,5-hydrogen shifts in **1**, **2c**, **3a**, and **3b**, given in Table 2, are consistent with the activation enthalpies that are provided in Table 1. The very modest effects of phenyl substituents both on the activation enthalpies in Table 1 for 1,5-hydrogen shifts in the cisoid conformers and on the bond lengths in Table 2 for the TSs show that the TS for 1,5-hydrogen shift in **1** is much less chameleonic than the TS for the Cope rearrangement of 1,5-hexadiene.

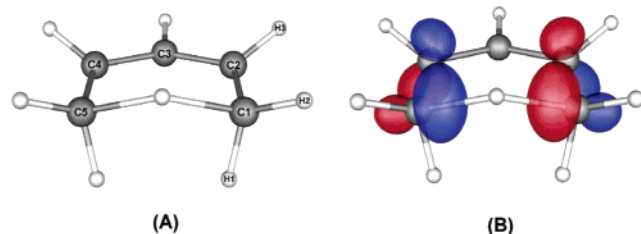
In addition to this general observation, the results in Tables 1 and 2 also provide some specific information about the electronic structure of the TS for a 1,5-hydrogen shift in **1**. Comparison of the geometry of the TS with that for 1,3-pentadienyl radical shows a reversal in the relative lengths of the C1–C2 and C2–C3 bonds. In the TS the C1–C2 bond is longer than the C2–C3 bond by 0.021 Å, whereas in the radical C1–C2 is shorter than the C2–C3 bond by 0.060 Å. Bonding of the hydrogen in the TS to C1 and C5 of pentadienyl radical lengthens the C1–C2 bond by 0.054 Å and shortens the C2–C3 bond by 0.027 Å.

The unequal C–C bond lengths in pentadienyl radical make the positive spin density at C3 greater than that at C1 and C5.<sup>23</sup> Therefore, to the extent that the carbon skeleton of the TS for a 1,5-hydrogen shift in **1** resembles pentadienyl radical, a phenyl substituent at C3 should provide the greatest stabilization of the TS. However, the results in Table 1 show that the TS for rearrangement of **2c** has the highest energy of the three monophenyl TSs and that the phenyl substituent at C3 actually makes the predicted activation enthalpy for rearrangement of cisoid **2c** 0.5 kcal/mol higher than that for rearrangement of unsubstituted cisoid **1**.

The pair of phenyl groups at C1 and C5 makes the activation enthalpy for rearrangement of **3a** 3.2 kcal/mol lower than that of **1**. This substituent effect could indicate that this pair of phenyl groups makes the carbon skeleton in the TS for rearrangement of **3a** more like that of a pentadienyl radical, because the radical has positive spin density at these two carbons, as well as at C3.<sup>23</sup> However, the C1–H bond length is only 0.003 Å longer in the TS for rearrangement of **3a** than in the TS for rearrangement of **1**, and the C–C bond lengths in the former TS are less pentadienyl-like than in the latter.

The 0.011 Å lengthening of the C1–C2 bond and the near constancy of the C1–H and C2–C3 bond lengths in the TS for rearrangement of **3a**, relative to those in the TS for rearrangement of **1**, are what one would expect from a contribution of

(23) (a) Sustmann, R.; Schmidt, H. *Chem. Ber.* **1979**, *112*, 1440. (b) Davies, A. G.; Griller, D.; Ingold, K. U.; Lindsay, D. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 633. (c) MacInnes, I.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1073. (d) Clark, K. B.; Culshaw, P. N.; Griller, D.; Lossing, F. P.; Martinho-Simoes, J. A.; Walton, J. C. *J. Org. Chem.* **1991**, *56*, 5535.



**Figure 6.** The geometry (A) and the HOMO (B) for the 1,5-hydrogen shift transition structure in 1,3-pentadiene. The H1–C1–C2–H3 dihedral angle is  $-131.0^\circ$ , but pyramidalization of C1 by  $34.5^\circ$  and C2 by  $-13.3^\circ$  makes the H2–C1–C2–H3 dihedral angle only  $6.7^\circ$ .

resonance structure **C** in Figure 5. The effects of the phenyl groups at C2 and C4 on the bond lengths in the TS for a 1,5-hydrogen shift in **3b** are also precisely those that one would expect for a contribution from resonance structure **C**. The phenyl groups in **3b** result in the C–H bond length being shorter and all of the C–C bond lengths being longer in the TS for rearrangement of **3b** than the comparable bond lengths in the TS for rearrangement of **1**.

Further evidence for a contribution from structure **C** in Figure 5 comes from the effect of the phenyl substituents on the enthalpies of the TSs for rearrangement of **3a** and **3b**, discussed in the previous section. As expected for a contribution from resonance structure **C**, but not from resonance structure **A** in Figure 5, the phenyl groups in both **3a** and **3b** stabilize the TS for 1,5-hydrogen shift, whereas the phenyl group at C3 in **2c** does not. This difference between the abilities of the phenyl groups to stabilize the TS is manifested in the finding that the C–Ph distances are  $0.005 \text{ \AA}$  shorter in the TSs for rearrangement of **3a** and **3b** than in the TS for rearrangement of **2c**.

Why does resonance structure **C** in Figure 3 apparently contribute considerably more than resonance structure **A** to the TS for a 1,5-hydrogen shift in **1**? The geometry of the TS, depicted in Figure 6, shows that, in order to bond to the migrating hydrogen, C1 and C5 must rotate toward this hydrogen, thus decreasing the overlap between C1 and C2 and between C4 and C5. The resulting disruption of the  $\pi$  conjugation causes the TS to resemble an allylic radical, plus a hydrogen atom bonded to C1 and C5 (structure **C**), much more than it resembles a pentadienyl radical plus a hydrogen (structure **A**).

We attribute the small rate retarding effect, predicted for a phenyl substituent at C3 in **2c**, to the finding that the TS for a 1,5-hydrogen shift in **1** resembles structure **C** in Figure 5, much more than structure **A**. In addition, the enthalpy of structure **A**,<sup>23b</sup> a pentadienyl radical plus a hydrogen atom, is nearly 50 kcal/mol higher than the TS for a 1,5-hydrogen shift in cisoid **1**.<sup>12,13,25</sup> Therefore, unlike the case in the Cope rearrangement, where diradical structures **A** and **C** in Figure 1 are, respectively, only about 11 and 26 kcal/mol above the chair TS,<sup>4b,24</sup> the ability of the phenyl substituent at C3 in **2c** to stabilize a localized radical center by 11–12 kcal/mol<sup>27</sup> has little effect on the electronic structure of the TS for a 1,5-hydrogen shift in **1**.

## Conclusions

The phenyl-substituent effects in **2** and **3** on the activation enthalpy for the 1,5-hydrogen shift in 1,3-pentadiene (**1**) are predicted to be sizable, ranging from an increase in  $\Delta H^\ddagger$  of 2.7 kcal/mol in **2a** to a decrease of 6.8 kcal/mol in **3b**. However, if differences between steric effects in the transoid isomers are factored out by comparing the activation enthalpies in the cisoid conformers, and if the exothermicity of the rearrangement of **2e** to **2a** is accounted for by replacing the activation enthalpy by the intrinsic barrier,<sup>22</sup> the electronic components of the phenyl-substituent effects are quite modest.

Each phenyl group in cisoid **2b**, **2d**, and **3b** lowers the activation enthalpy from that in cisoid **1** by ca. 1 kcal/mol. Because an unconjugated phenyl group in **2e** and **3a** becomes conjugated in the TS, the phenyl-substituent effects on the 1,5-hydrogen shifts in the cisoid conformers are slightly larger in **2e** and **3a** than in **2b**, **2d**, and **3b**. The phenyl group in cisoid **2e** lowers the intrinsic barrier height by 1.5 kcal/mol, and the pair of phenyl groups in cisoid **3a** lowers the intrinsic barrier height by about twice as much.

Nevertheless, comparison of the relative energies of the TSs reveals that the phenyl groups in **2b**, **2d**, and **3b** provide about 0.5 kcal/mol more stabilization for the TSs than do the phenyl groups in **2a**, **2e**, and **3a**. In contrast, the phenyl group at C3 is calculated to make the TS for the degenerate rearrangement of **2c** 1.8 kcal/mol higher than that for the 1,5-hydrogen shift that equilibrates **2b** and **2d**. In fact, a C3 phenyl group is actually predicted to make the activation enthalpy for a 1,5-hydrogen shift 0.5 kcal/mol higher in cisoid **2c** than in cisoid **1**.

The calculated effects of the phenyl substituents on the activation enthalpies and TS geometries indicate that the dominant diradical resonance structure that contributes to the TS is not a pentadienyl radical plus a hydrogen atom (structure **A** in Figure 5) but an allylic radical at C2–C3–C4, plus a hydrogen atom bonded to C1 and C5 (structure **C** in Figure 5). The dominance of resonance structure **C** is attributed to the necessity of C1 and C5 twisting partially out of conjugation with the allylic radical at C2–C3–C4, in order to bond to the migrating hydrogen, as well as to the ca. 20 kcal/mol lower energy of structure **C**, as compared to structure **A**.<sup>25</sup>

Unlike the case in the Cope rearrangement,<sup>3,4</sup> our calculations do not reveal a strong variability of the geometry of the TS for a 1,5-hydrogen shift in **1** with number and placement of phenyl substituents. However, if the migrating hydrogen in **1** were replaced by a group that afforded a much smaller enthalpy difference between the TS for concerted 1,5 shift and the diradical analogous to **C**, it seems possible that the TS would become more chameleonic in nature, especially in exhibiting an increased response to a phenyl substituent at C3. Whether this does, in fact, prove to be the case must await further computational and/or experimental studies of concerted [1,5]-sigmatropic shifts with migrating groups other than hydrogen.

**Acknowledgment.** We thank the National Science Foundation for supporting this research and Professor William von Eggerts Doering for suggesting it to us. S.H. thanks Tottori University

(24) Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

(25) Assuming that resonance structure **C** in Figure 5 represents the transfer of a hydrogen atom from C1 to C5 in the nodal plane of the allylic radical, Doering has used thermochemistry to estimate that this structure lies only a little more than 30 kcal/mol above the TS for a concerted 1,5-hydrogen shift in **1** and ca. 20 kcal/mol below the pentadienyl radical plus hydrogen atom in resonance structure **A**.<sup>26</sup> B3LYP/6-31G\* calculations give similar results, placing diradical **C** 27.7 kcal/mol above the TS and 20.1 kcal/mol below pentadienyl radical plus a hydrogen atom.

(26) Doering, W. von E.; Keliher, E. J.; Zhao, X., manuscript submitted for publication. We are indebted to Professor Doering for sending us a preprint.

(27) (a) Hrovat, D. A.; Borden, W. T. *J. Phys. Chem.* **1994**, *98*, 10460. (b) Ellison, G. B.; Davico, G. E.; Birnbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrom. Ion Processes* **1996**, *156*, 109.

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**Supporting Information Available:** Optimized B3LYP/6-31G\* geometries and energies for the transoid and cisoid

conformations of **1**, **2a–e**, and **3a** and **b** and for the TSs for a 1,5-hydrogen shift in each of these 3-(Z)-1,3-pentadienes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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