Perturbations by Phenyl on the 1,5-Hydrogen Shift in 1,3(*Z*)-Pentadiene. Another Chameleonic Transition Region?

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Abstract: The acyclic 1,5-dienyl hydrogen shift is accelerated by radical-stabilizing phenyl substituents without regard to the type of position occupied in the 1,3(*Z*)-pentadiene system. 1-Phenyl-5-*p*-tolyl-1,3(*Z*)-pentadiene has a corrected energy of activation 5.8 kcal mol^{-1} lower than that of the parent, while the 2- and 3-phenyl analogues, examined in cyclic systems specifically designed to obviate the otherwise general need for a thermochemical correction to the immediately precursory *s-cis* conformation, reveal stabilizing effects of 3.6 and 3.4 kcal mol^{-1}, respectively. These relatively small effects are consistent with a chameleonic conceptual scheme for the transition region.

Introduction

The acyclic 1,5-dienyl hydrogen shift in penta-1,3(*Z*)-dienes,[1] one of the more prominent among purely thermal rearrangements, may provide another example of chameleonic behavior. An earlier example, revealed experimentally in Cope's concerted rearrangement of hexa-1,5-dienes (Figure 1),[2] has been given theoretical support by the calculations of Hrovat, Beno, Lange, Yoo, Houk, and Borden.[3]

The transition region of the acyclic 1,5-dienyl hydrogen shift can be represented as a continuum between the two extremes in Figure 2, one end being characterized by *coplanarity* of the hydrogen atoms of the 1 and 5 methylene groups with a planar pentadienyl skeleton,[4] the other end, by their *orthogonal* orientation. That the transition region in the paradigm is well approximated by the central drawing in Figure 2 has been supported by several theoretical investigations, to all of which references are made in the publication of Hess and Baldwin.[5] Under the chameleonic hypothesis, perturbation by radical-stabilizing groups in positions 2 and/or 4 may move the transition region toward the allyl end of the continuum (lower drawing) or toward the pentadienyl end (upper drawing) when occupying position 3. The core element responsible for the large energy of concert of the rearrangement consists of the migrating hydrogen atom being bonded by its 1s orbital to orbitals of the
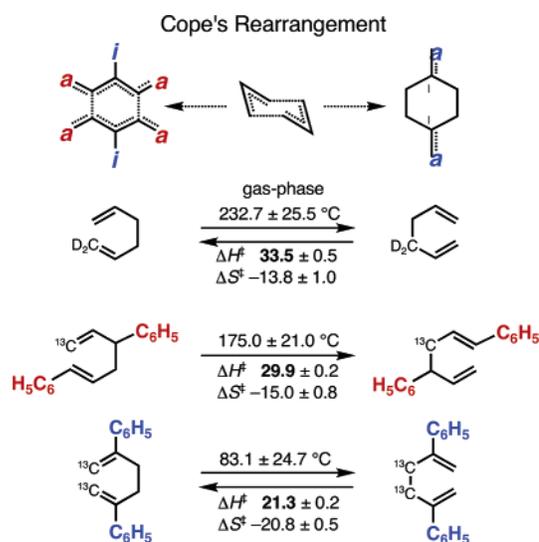
Figure 1. Perturbations by phenyl groups on the activation parameters of Cope's rearrangement as a function of occupancy at active positions (red "a") in a hypothetical bis-allylic transition region and at active, secondary radical positions (blue "a") in a cyclohexadiyl transition region. Enthalpies of activation are reported in kcal mol^{-1}.

giving and receiving 1 and 5 methylene groups.[6,7] These can be hybridized throughout the continuum between sp^2 (planar, trigonal) and sp^3 (pyramidal, tetrahedral).

Crucial to the testing of the chameleonic model is a comparison of radical-stabilizing groups, phenyl in this work, at the 2- and 3-position. The effect is expected to be comparable to that found in the Cope rearrangement disubstituted in positions 1 and 4 in which the transition region has moved

(1) Thorough reviews are found in Alubugin, I. V.; Monoharan, M.; Breiner, B.; Lewis, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 9329−9342, in Hess and Baldwin,[5] and in Dieter Hasselmann, Houben-Weyl, *Methods of Organic Chemistry*; Thieme: Stuttgart, 1995; Vol. E 21d, 4421−4430.

(2) Doering, W. v. E.; Wang, Y.-h. *J. Am. Chem. Soc.* **1999**, *121*, 10112−10118.

(3) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, H.-y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 10529−10537.

(4) This end of the continuum is unacceptably high in energy owing to the hydrogen atom−hydrogen atom interpenetration of their van der Waals radii and is not as easily acceptable as either of the two ends of the continuum presented in Cope's rearrangement. This end of the continuum, perhaps better reflected in cyclopentadiene, hypothetically the dehydrogenation product of *s-cis*-1, 3(*Z*)-pentadiene, has an activation energy for intramolecular 1,5-hydrogen shift of E_a 25 kcal mol^{-1}.

(5) Hess, B. A., Jr.; Baldwin, J. E. *J. Org. Chem.* **2002**, *67*, 6025−6033.

(6) The parent model for the 1,5-hydrogen shift is the transfer of a hydrogen atom between methane and a methyl radical. A closer analogy would be the uninvestigated transfer from the methyl group of propene to an allyl radical.

(7) (a) Ma, X.-l.; Schobert, H. H. *Ind. Eng. Chem. Res.* **2003**, *42*, 1151−1161. (b) Camaioni, D. M.; Autrey, S. T.; Salinas, T. B.; Franz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 2013−2022.
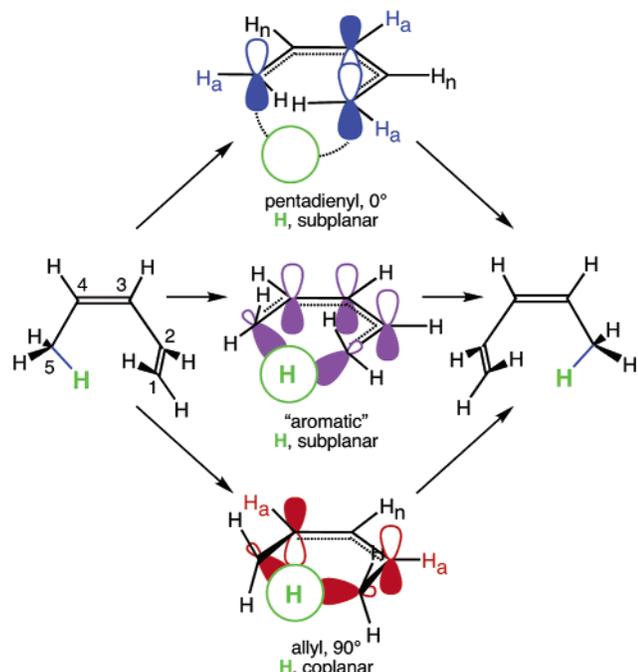
Figure 2. Two extreme representations of the transition region of the 1,5-hydrogen shift: the upper depicting the active 3-position in a pentadienyl extreme, the lower depicting the active 2- and 4-positions in an allyl extreme; the upper showing C1 and C5 as pure sp^2, the lower as sp^3.

toward the allylic end of the continuum. The small effect, 3.7 kcal mol^{-1}, is comparable to the extra stabilization of ~3 kcal mol^{-1} given to an allyl radical by phenyl (as in the cinnamyl radical) in the more transparent cis−trans thermal rearrangement of a double bond.[8] That given to a pentadienyl radical by phenyl in the 3-position can hardly be much greater but has not been independently evaluated.

The acyclic version of the 1,5-dienyl hydrogen shift was first uncovered by Enklaar in the thermal conversion of ocimene to alloöcimene[9] and generalized by Wolinsky in 1962.[10] His proposed mechanism, "a six-membered transition state in which five carbon atoms lie in a plane or near the plane with the migrating hydrogen above or below this plane," was later legitimized theoretically by Woodward and Hoffmann in 1965[11] and given elegant experimental confirmation by Roth, König, and Stein in 1970.[12c]

An early kinetic study by Roth and König of the unsubstituted paradigm, 1,3(Z)-pentadiene, its degeneracy broken by deuterium-labeling, provided the Arrhenius parameters, $E_a = (36.1 \pm 2.2)$ kcal mol^{-1} and $\log A = (11.34 \pm 1.0)$.[12a,13] An energy of concert derived by comparing this experimental energy of activation with that of a nonconcerted model consisting of a free hydrogen

atom and a pentadienyl radical in its U configuration can be estimated at ~48 kcal mol^{-1}, a value that places the 1,5-dienyl hydrogen shift among the most strongly concerted of the thermal organic chemical rearrangements.

Perturbational Approach

A traditional approach to conceptualizing a transition region relies on the response of a paradigm to perturbations by substituents known to stabilize or destabilize simple intermediates. Recall the carbenium ion, the carbanion, and, as thought relevant here, the free radical. In two unpublished dissertations, one by Norbert Rohse,[14] the other by Monika Schlief,[15] both under the guidance of the late Professor Wolfgang R. Roth, the first systematic applications of the perturbational approach to the 1,5-hydrogen shift have been conducted. Their studies have been guided by the Dewar model of a planar pentadienyl radical as transition region, in which polarization toward a pentadienyl carbanion/proton, resonance contributor determines the response to substituents.[16] Of the two types of position, 1 and 5 and 3, both active under this mechanistic hypothesis, substituents at the 3-position have been the focus of Rohse's investigations (see the upper representation in Figure 2). Substitution at the C3-position by F, OCH$_3$, Cl, H, CN, CH$_3$, C$_6$H$_5$, CF$_3$, and COOCH$_3$ encompasses relative rate constants at 200 °C ranging from 0.57 to 13.4 ($H = 1.0$). The Arrhenius parameters for this series are reproduced in Table SI-1 of the Supporting Information. DFT-based predictions by Saettel and Wiest of energies of activation for the *s-cis* conformations of 1,3(Z)-pentadiene ($E_a = 32.9$ kcal mol^{-1}) and its 3-methoxy ($E_a = 32.4$ kcal mol^{-1}), and 3-fluoro ($E_a = 33.5$ kcal mol^{-1}) derivatives[17] cannot be convincingly compared with the experimental results of Rohse on related *s-trans* conformations of hexa-1,3(Z)-diene ($E_a = 32.8$ kcal mol^{-1}),and its 3-methoxy ($E_a = 33.4$ kcal mol^{-1}) and 3-fluoro ($E_a = 32.7$ kcal mol^{-1}) derivatives.[14]

Kinetic data and derived Arrhenius parameters for a large number of alkyl-substituted *acyclic* 1,3(Z)-pentadienes have been in the literature for several decades (see Figures 4, 5, and SI-1). Their comparison with the unsubstituted paradigm might be expected to provide one test of the chameleonic conceptual scheme. However, the radical-stabilizing power of alkyl groups is small at best (the difference in bond dissociation energies of primary and secondary C−H bonds, for example, being 2.4 kcal mol^{-1}).[18] Comparisons are further complicated by experimental activation energies that relate to the almost invariably more stable, hydrogen-shift-incompetent, *s-trans* conformations of the 1,3(Z)-pentadienes, not to the *s-cis* conformations, which are uniformly accepted to be the shift-competent, *immediate* starting points for the rearrangement.[19] This complication can be seen

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(9) Enklaar, C. J. *Recl. Trav. Chim. Pays-Bas* **1907**, *26*, 157−179.
(10) Wolinsky, J.; Chollar, B.; Baird, M. D. *J. Am. Chem. Soc.* **1962**, *84*, 2775−2779.
(11) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511−2513.
(12) (a) Roth, W. R.; König, J. *Liebigs Ann. Chem.* **1966**, *699*, 24−32. (b) Roth, W. R *Chimia* **1966**, *20*, 229−264. (c) Roth, W. R.; König, J.; Stein, K. *Chem. Ber.* **1970**, *103*, 426−439.
(13) Recalculation from the specific rate constants given on the last page of ref 12a leads to the following Arrhenius parameters (standard error; temperature range, 185−205 °C): for k_H, $E_a = (36.13 \pm 2.16)$ kcal mol^{-1}, $\log A = (11.35 \pm 1.0)$ (Houk, Li, and Evanseck[36d] report identical values, and may be presumed to have carried out the same recalculations) and for k_D, $E_a = (37.7 \pm 0.7)$ kcal mol^{-1}, $\log A = (11.36 \pm 0.3)$. Unjustified recalculation of k_H without the 190.2° point improves matters, $E_a = (34.83 \pm 0.78)$ kcal mol^{-1}, $\log A = (11.75 \pm 0.37)$, but lowers the energy of activation by 1.3

kcal mol^{-1}! Extrapolation of the values of k_H/k_D at the three temperatures given (°C), 195.1°, 5.22; 200.0°, 4.97; 205.3°, 5.11, to 25 °C is not justifiable. This footnote may be of interest to the several theoretical chemists who have been stimulated by this apparently large deuterium isotope effect.
(14) Rohse, N. Substituenteneffekte auf die 1,5-Pentadienylwasserstoff-verschiebung, PhD Dissertation, Abteilung für Chemie der Ruhr-Universität, Bochum, Germany (Roth, W. R, research sponsor), 1986.
(15) Schlief, M. Substituenteneffekte auf die 1,5-Pentadienylwasserstoff-verschiebung in Cycloheptatrien, PhD Dissertation, Abteilung für Chemie der Ruhr-Universität, Bochum, Germany (Roth, W. R, research sponsor), 1990.
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(17) Saettel, N. J.; Wiest, O. *J. Org. Chem.* **2000**, *65*, 2331−2336.
(18) Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347−1353.
(19) Carpenter, J. E.; Sosa, C. P. *THEOCHEM* **1994**, *311*, 325−330.
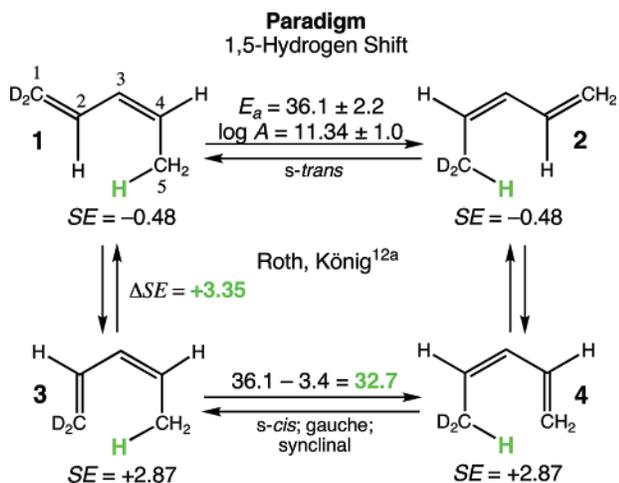
Figure 3. Experimental activation parameters for the simplest, paradigmatic 1,5-hydrogen shift in the more stable *s-trans*,penta-1,3(*Z*)-diene are shown along with the hypothetical energy of activation of the rearrangement-competent *s-cis* conformation, estimated from the MM2-calculated, steric energy difference. Error limits are standard errors; thermochemical quantities in kcal mol^{-1}.

already in the paradigm (Figure 3). The ideal correction required to extract the activation parameters for rearrangement of the *s-cis* conformation from the *s-trans* related, experimental values (e. g., **3** to **4** in Figure 3) is the difference between their enthalpies and entropies of formation. These are not experimentally accessible. In their stead, we have used the difference in the steric energies (ΔSE) calculated for the two conformations by the molecular mechanics program, MM2, of Allinger as made available in Chem 3D Pro 5.[20]

With 1,3(*Z*)-pentadiene as example, the calculated value of ΔSE is +3.35 kcal mol^{-1} and leads to a corrected energy of activation for the 1,5-hydrogen shift from the *s-cis* conformation of 32.7 (36.1−3.4) kcal mol^{-1}. Saettel and Wiest, and most recently, Hayase, Hrovat, and Borden, have used the density functional theory of B3LYP, to calculate the difference in enthalpies of formation of the two conformations and have, reassuringly, found values of 3.7 and 3.6 kcal mol^{-1}, respectively.[17,21] The base value of 32.7 kcal mol^{-1} for the paradigm is used in the following comparisons with the conformationally corrected values of the perturbed systems (but please note again the gnawing reservation implied in ref 13).

A second complication in making the comparisons arises from interactions of the substituents with carbon−carbon double bonds, the so-called energy of conjugation or conjugative interaction. This is a perturbation on the educt, irrespective whether taken as *s-trans* or *s-cis*. In the domain of alkyl groups, values for conjugative interaction of methyl groups have been proposed in Figure 1 of Doering et al.[22] They range between −2.66 and −0.87 kcal mol^{-1} depending on the total degree of substitution. We hesitate to apply this type of correction to the alkyl perturbations because the radical-stabilizing power of alkyl groups is comparable in magnitude to the conjugative interaction operating in the educt. What fraction of the conjugative interactions may already be contained in the calculated steric energy of the educt is also unknown.

Figure 4. Depicted are 1,5-hydrogen shifts in the more stable *s-trans* conformations of two methyl-substituted 1,3(*Z*)-pentadienes designated by the symbol, for example, (5 ⟷ 1), to indicate the reversible rearrangement of the substituent between the 5- and 1-positions. Heats of formation, $\Delta_f H°$, are derived by Benson's method of group equivalent values (cf. caption of Figure 3 for additional explanations).

Perturbation at the 5(1)[23] position by unconjugated methyl[14,15,24] (Figure 4) or ethyl[25] (Figure SI-1) lowers the conformationally corrected energy of activation by −3.2 kcal mol^{-1} in both instances. We make an exception and suggest that much of the 2.7-kcal mol^{-1} conjugative interaction of alkyl in the *trans*-1,2-disubstituted olefins ultimately destined to become the products, 1(*E*)-alkyl-3(*Z*)-pentadienes, may already be making itself felt in the transition region. In this connection, examination of 1,5-dimethyl-1(*E*),3(*Z*)-pentadiene might be illuminating, the more so since Hess and Baldwin have predicted, also by B3LYP, that it should have the same energy of activation as that of the unsubstituted paradigm (uncorrected for the *s-trans*/*s-cis* conformational difference).[5]

Perturbations by methyl[26] or ethyl[27] at the 2(4)-position, or by two methyl groups at the 2,3(4,3)-positions,[28] do not significantly lower the conformationally corrected energies of activation (−0.2, +1.0, and −0.5 kcal mol^{-1}, respectively; Figures 5 and SI-1). Unfortunately lacking, but perhaps under-

(20) CambridgeSoft Corporation, 100 CambridgePark Drive, Cambridge, MA 02140: ChemBats3D PRO, version 5.0.
(21) Hayase, S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2004**, *126*, 10028−10034.

(22) Doering, W. v. E.; Benkhoff, J.; Carleton, P. S.; Pagnotta, M. *J. Am. Chem. Soc.* **1997**, *119*, 10947−10955.
(23) As a short-hand, idiosyncratic notation expressing the two positions between which substituents are distributed by the reversible 1,5-hydrogen shift; 5(1), for example, indicating reaction from the educt, 1(5) indicating the reverse reaction of the product.
(24) Frey, H. M.; Pope, B. M. *J. Chem. Soc. A* **1966**, 1701−1702.
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(26) (a) Frey, H. M.; Ellis, R. J. *J. Chem. Soc. A* **1965**, 4770−4773. (b) Glass, D. S.; Boikess, R. S.; Winstein, S. *Tetrahedron Lett.* **1966**, 999−1008.
(27) Frey, H. M.; Solly, R. K. *J. Chem. Soc. A* **1969**, 733−735.
(28) Frey, H. M.; Lamont, A. M.; Walsh, R. *J. Chem. Soc. A* **1971**, 2642−2646.
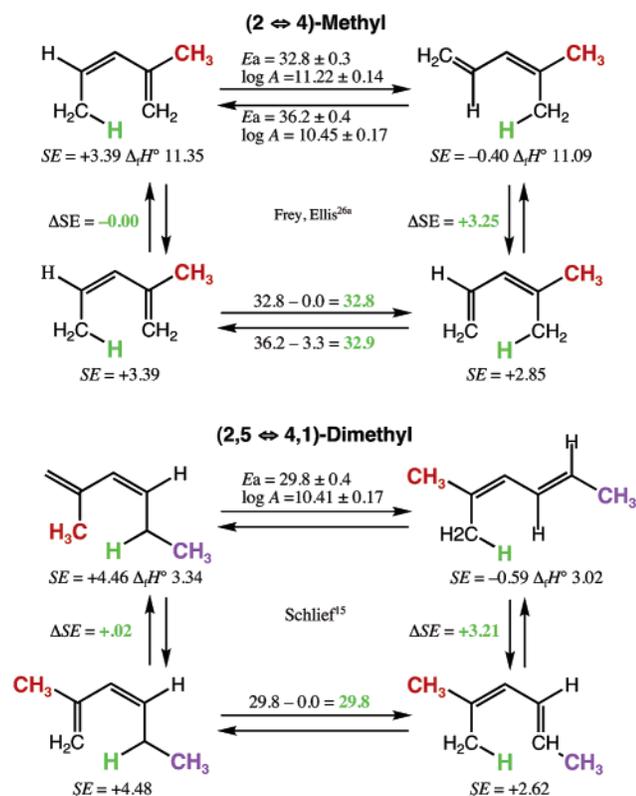
Figure 5. Depicted are the 1,5-hydrogen shifts of two additional methyl-substituted 1,3(Z)-pentadienes (cf. captions of Figures 3 and 4 for additional explanations).

standably so in view of its symmetry, is a datum for 3-methyl-1,3(Z)-pentadiene. Data are available, however, for 2,3(4,3)-dimethyl-1,3(Z)-pentadiene ($+0.5$ kcal mol^{-1}; Figure SI-1) and 3,5(3,1)-dimethyl-1,3(Z)-pentadiene (-2.2 kcal mol^{-1} when compared to the unsubstituted paradigm, but $+0.9$ kcal mol^{-1} when compared, in our opinion more appropriately, to 5(1)-methyl-1,3(Z)-pentadiene) (Figure 4).[14,28] Although methyl groups in the 2- or 3-position do not appear to stabilize the transition region, a methyl group in the sp^3 5-position on its way to becoming an sp^2 1-position in the product makes a significant contribution of 3.1 kcal mol^{-1}, commensurate with its developing energy of conjugation.

Perturbation by the Ad Libitum Phenyl Group

Perturbation by strongly radical-stabilizing phenyl groups seems more likely to lead to definitive conclusions. Four examples have been examined in Roth's laboratory. These are shown in Figures 6 and 7, along with their calculated, *SE* conformational corrections. Perturbation by a single phenyl group at the 2(4)-position lowers the corrected energy of activation energy by 3.2 kcal mol^{-1}, while a phenyl group at the 2(4)-position coupled with a methyl group at the 5(1)-position has a lowering effect of 5.2 kcal mol^{-1} vis-à-vis the corrected unsubstituted paradigm or 2.1 kcal mol^{-1} vis-à-vis 5(1)-methyl-1,3(Z)-pentadiene.[15] The combination of 4(2)-phenyl and 5(1)-methyl has an energy-raising effect of $+0.7$ kcal mol^{-1}, probably owing to adverse steric interactions.[15]

There being no simple 3(3)-phenyl analogue, the disubstituted 3(3)-phenyl-5(1)-methyl must serve as the only representative. Its lowering effect vis-à-vis the unsubstituted paradigm is 3.2 kcal mol^{-1}, the same as that of the 2(4)-phenyl analogue.[14] But
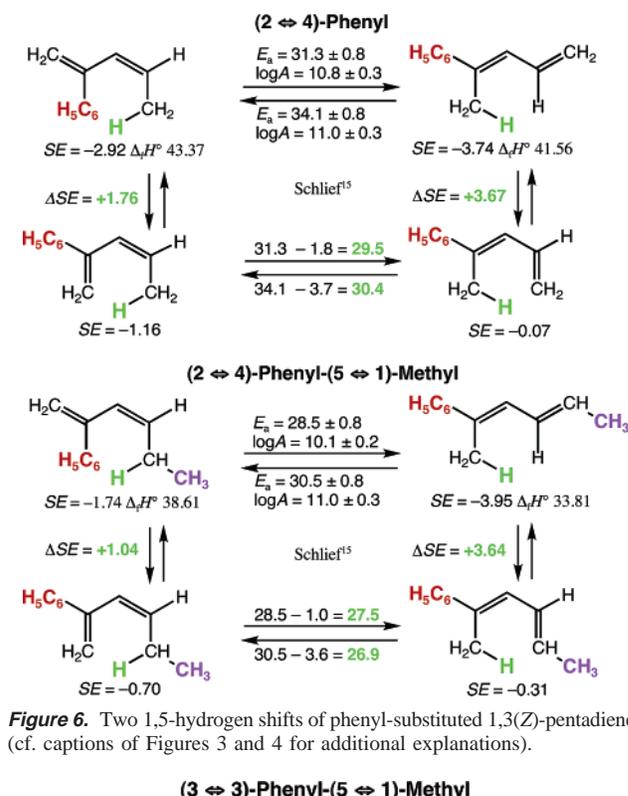
Figure 6. Two 1,5-hydrogen shifts of phenyl-substituted 1,3(Z)-pentadienes (cf. captions of Figures 3 and 4 for additional explanations).
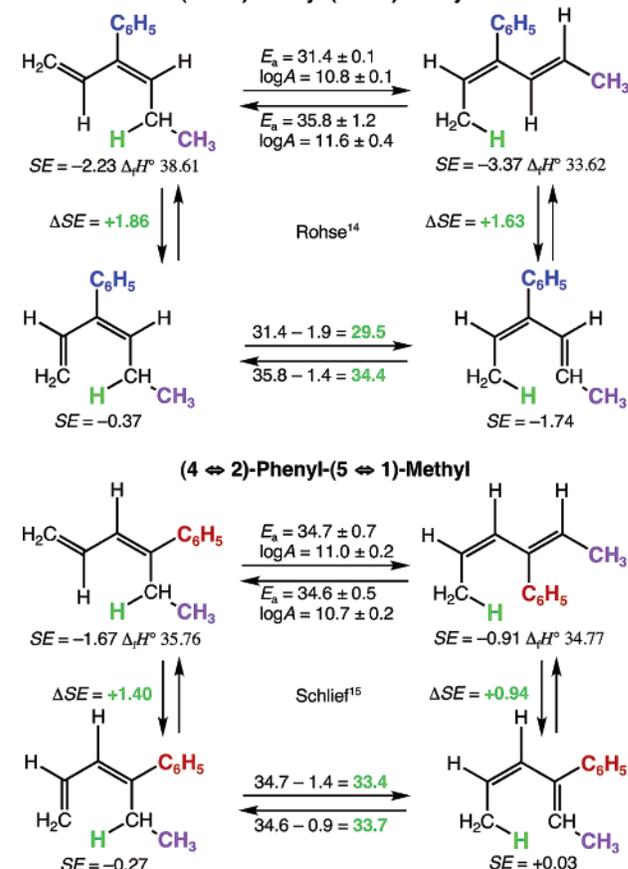
Figure 7. Two further 1,5-hydrogen shifts of phenyl-substituted pentadienes (cf. caption of Figures 3 and 4 for additional explanations).

once again, compared, perhaps more appropriately, to 5(1)-methyl-1,3(Z)-pentadiene (Figure 4), the value drops to -0.1 kcal mol^{-1}. Investigation of the degenerate 3(3)-phenylpenta-

1,3(Z)-diene for direct comparison with 2(4)-phenylpenta-1,3-(Z)-diene would give a more convincing insight into the relative importance of a phenyl group at the 2- and 3-position.

Correction for conjugative interaction by phenyl would lower the estimated heat of formation of the educt and, taken alone, should manifest itself as a higher energy of activation than would otherwise be observed if the perturbation had *no* effect on the heat of formation of the educt. The magnitude of the conjugative interaction of an ad libitum phenyl group located at the otherwise unsubstituted α-position of a styrene has been estimated to be 5.1 kcal mol^{-1}, or 2.5 kcal mol^{-1} if located at an already substituted β-position.[22] Although the reliability of the application of these values to butadienes has not been demonstrated, they must serve if any corrections for conjugative interaction in the educt seem advisable.

In the examples of Figures 6 and 7, phenyl groups are free to assume whatever conformation is energetically most favorable in the incompetent *s-trans* educt, the competent *s-cis* educt, and the fleeting transition region; that is, these phenyl groups are what we call ad libitum. They are all of the β-type and therefore subject to the correction of 2.5 kcal mol^{-1}. Thus, the single phenyl group in 2(4)-phenyl-1,3(Z)-pentadiene (Figure 6) may be corrected not only by the 1.8-kcal mol^{-1} difference in steric energy but by a conjugative interaction of 2.5 kcal mol^{-1}. The result is a total stabilization in the transition region of 5.7 kcal mol^{-1}.[21,29] 2(4)-Phenyl-5(1)-methylpenta-1,3(Z)-diene (Figure 6) leads to a stabilization of 7.7 kcal mol^{-1} (32.7−27.5 + 2.5 kcal mol^{-1}) vis-à-vis the corrected paradigm or 4.6 kcal mol^{-1} (29.6−27.5 + 2.5 kcal mol^{-1}) vis-à-vis the corrected value for 5(1)-methylpenta-1,3(Z)-diene (Figure 4).

3(3)-Phenyl-5(1)-methylpenta-1,3(Z)-diene (Figure 7) leads to a stabilization of 5.7 kcal mol^{-1} (32.7−29.5 + 2.5 kcal mol^{-1}) vis-à-vis the corrected paradigm or 2.6 kcal mol^{-1} (29.6−29.5 + 2.5 kcal mol^{-1}) vis-à-vis the corrected value for 5(1)-methylpenta-1,3(Z)-diene (Figure 4).

We conclude from these examples from the literature that perturbation by phenyl in either the 2- or the 3-position occasions a small lowering in the conformationally corrected energies of activation. The firmness of the conclusion is compromised by uncertainties in the accuracy of the corrections, the magnitudes of which are comparable to expected π-electronic stabilizations.

Present Experimental Results

Perturbation by phenyl at the 1- or 5-position has not been reported heretofore in the literature. This lacuna, the more acute since, from the analysis outlined in Figure 2, an energy-lowering interaction is predicted throughout the hypothetical continuum of transition regions, is now filled by examination of the reversible system, 1-phenyl-5-*p*-tolylpenta-1(E),3(Z)-diene [(**E,Z**)-**5**] and 1-*p*-tolyl-5-phenylpenta-1(E),3(Z)-diene [(**E,Z**)-**6**] (Figure 8). If not as pristinely degenerate as 1,5-diphenyl-1(E),3(Z)-pentadiene, (**E,Z**)-**5** and (**E,Z**)-**6** involve no more than a trivial difference in their heats of formation.

Preparation of (**E,Z**)-**5** from *trans*-cinnamaldehyde and triphenyl-β-*p*-tolylethylphosphonium bromide proceeded according

(29) In a recent publication,[21] Hayase, Hrovat and Borden calculate by B3LYP values of $\Delta H^{\ddagger} = 30.3$ and 34.5 kcal mol^{-1}, respectively, for the forward and reverse rearrangements. These compare with 30.4 and 33.1 kcal mol^{-1} obtained experimentally by Schlief (Roth).[15] Her measurements of equilibrium constants over the temperature range, 238.1−277.7 °C lead to a value for $\Delta\Delta H° = -2.78 \pm 0.14$ kcal mol^{-1} (HHB: −4.2 kcal mol^{-1}).

(1 ⇔ 5)-Phenyl-(5 ⇔ 1)-*p*-Tolyl

Figure 8. Interconversion of 1-phenyl-5-*p*-tolyl-1,3(Z)-pentadiene, (**E,Z**)-**5**, and 1-*p*-tolyl-5-phenyl-1,3(Z)-pentadiene, (**E,Z**)-**6**. Error limits are at the 95% confidence level.

Table 1. Specific Rate Constants for the Interconversion of 1-Phenyl-5-*p*-tolylpenta-1,3(Z)-diene [(**E,Z**)-**5**] and 1-*p*-Tolyl-5-phenylpenta-1,3(Z)-diene [(**E,Z**)-**6**]

educt	$k_1{}^a$	K	educt	$k_1{}^a$	K
	153.7 °C			185.2 °C	
(**E,Z**)-**5**	5.35 ± 0.04^b	1.257	(**E,Z**)-**5**	63.0 ± 0.6^b	1.233
(**E,Z**)-**6**	5.29 ± 0.06^b		(**E,Z**)-**6**	61.2 ± 0.9^b	

Arrhenius Parameters
$E_a = 30.10 \pm 0.21 \ (\pm 0.92)^b$ kcal mol^{-1}; log $A = 10.14 \pm 0.11 \ (\pm 0.91)^b$
$\Delta H^{\ddagger} = 29.2 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -14.9 \pm 0.5$ eu.

$^a k_1 \times 10^{-6}$ sec^{-1}. ^{b} Error limits at the 95% confidence level.

to precedent. The resulting mixture of (E,E)-**5** and the desired (**E,Z**)-**5** resisted separation to a point where its necessity was questioned. Indeed the (E,E) isomer proved stable to heating at 200 °C, a temperature well above that required for study of the kinetics of the 1,5-hydrogen shift in the (E,Z) isomer. The unseparated (E,E) isomer could thus serve as an internal standard. To our pleased surprise, rearrangement of the system could be followed quantitatively by NMR spectroscopy. There seeming to be little serious question about the first-order nature of the forward and backward steps of the rearrangement, determination of the kinetics at two temperatures ($\Delta T = 31.5$ °C) was deemed likely to furnish more reliable Arrhenius parameters than allocating the two of the four runs to intermediate temperatures. The data relating relative concentrations and time of reaction are given in Table SI-2 of the Supporting Information. Specific rate constants were calculated on the basis of the standard equation for reversible first-order reactions. Values of the equilibrium concentration, x_e, were varied to achieve a "best fit". The means of the pairs of the x_e values at each temperature were then used to calculate the four specific rate constants reported in Table 1. Equilibrium constants at 153.7 °C and 185.3 °C are 1.250 and 1.233, respectively. This slight favoring at equilibrium of the *p*-methylstyryl isomer **6** over the styryl **5** is consistent with the observations of Bushby and Farber on related systems.[30] Arrhenius parameters for k_1 (**5** → **6**) are derived from the four specific rate constants in Table 1: $E_a = 30.1 \pm 0.2 \ (\pm 0.9)$ kcal mol^{-1}, log $A = 10.14 \pm 0.11 \ (\pm 0.9)$ [± standard errors (± 95% confidence levels)]; $\Delta H^{\ddagger} = 29.2 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -14.9 \pm 0.5$ eu.[31]

(30) Bushby, R. J.; Farber, A. M. *J. Chem. Soc., Perkin Trans.* II **1976**, 1695−1700.

Figure 9. 1,5-Hydrogen shifts in three cyclic 1,3(*Z*)-pentadienes restricted to *s-cis* conformations are shown. Error limits are at the 95% confidence level; thermochemical quantities in kcal mol⁻¹.

In the second part of this work, the need for a conformational correction to the experimental enthalpies of activation is removed. Systems specifically designed to be frozen in the *s-cis* conformation are realized by incorporating C2 and C3 of the basic *s-cis*-1,3(*Z*)-pentadiene system into a cyclohexane ring and fusing benzene rings to generate compounds **10** and **13** of Figure 9. The phenyl groups are simultaneously restricted to a geometry more nearly coplanar with the five atoms of the rearranging pentadiene and are no longer ad libitum.

The unsubstituted parent of this pair is 1(*Z*)-ethylidene-2-methylenecyclohexane (**7**). Its synthesis takes off from (*E*)-2-

Table 2. Specific Rate Constants for the Thermal Rearrangement of (*Z*)-2-Ethylidene-1-methylenecyclohexane, **(Z)-7**, to 1-Methyl-2-vinylcyclohexene (**8**)

temp, °C	$k_1{}^a$	temp, °C	$k_1{}^a$
117.9	5.86	165.1	40.5
117.9	5.60	165.1	40.4
121.6	7.60	175.7	116.
121.6	7.60	175.7	112.
131.7	27.5	185.7	193.
131.7	27.0	185.7	185.
		185.8	209.
		185.8	201.

Arrhenius Parameters
$E_a = 30.62 \pm 0.18 \ (\pm 0.40)^b$ kcal mol⁻¹; $\log A = 10.85 \pm 0.09 \ (\pm 0.20)^b$
$\Delta H^{\ddagger} = 29.8 \pm 0.2$ kcal mol⁻¹; $\Delta S^{\ddagger} = -13.0 \pm 0.5$ eu.

ᵃ $k_1 \times 10^{-6}$ sec⁻¹. *ᵇ* Error limits at the 95% confidence level.

ethylidenecyclohexan-1-one, prepared according to Van-Catledge from cyclohexanone and acetaldehyde.[32] Irradiation in degassed benzene generates a 0.9:1 mixture of (*Z*)- and (*E*)-2-ethylidenecyclohexan-1-one. Without separation, this mixture is converted by treatment with Wittig's reagent to a 1:0.8 mixture of (*E*)-**7** and (*Z*)-**7**, which can be separated by preparative GC.

Rates of rearrangement of **7** to 1-methyl 2-vinylcyclohexene (**8**) (Figure 9) in benzene-d_6 are determined at six temperatures over the range of temperatures, 117.8 to 185.7 °C. The product has the same NMR spectrum in CDCl₃ as that reported by Kabalka et alii.[33] Assignment of structure to compound **8** is based on its NMR spectrum and method of preparation. Quantitative analysis of mixtures of **7** and **8** is accomplished by NMR employing resonances at 5.27 and 6.89 ppm, respectively. The unrefined data relating time of reaction and relative concentrations are collected in Table SI-3 of the Supporting Information. Because the equilibrium constant relating **7** and **8** strongly favors **8**, the data can be translated into specific rate constants by a first-order model as well as by the model for reversible first-order reactions. In one variant of the latter, the value of the relative concentration at equilibrium x_e is varied to achieve a best fit for the specific rate constants; in another, the mean value, 0.9800, of the "best fit" values for x_e (there is no discernible trend with temperature) is then used in the calculation of the rate constants ($k_1 + k_{-1}$). From these rate constants (recorded in Table 2 and Figure 9), Arrhenius parameters are calculated:[34] $E_{k1} = 30.62 \pm 0.18 \ [\pm 0.40 \ (95\%)]$ kcal mol⁻¹ and log A 10.85 $\pm$ 0.09 [$\pm$ 0.20 (95%)] (translates at a mean temperature of 425 K into $\Delta H^{\ddagger} = 29.8$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -11.6$ cal deg⁻¹ mol⁻¹).

Sufficient **8** is recovered from the combined products of several kinetic experiments to provide material for a single kinetic run. At 185.6−186.0 °C, a sample of **8** containing 0.9% of **7** lead to 1.5% of **7** after 30 min and 2.5% after 60 min. A rough specific rate constant, $k_{-1} = 2.6 \times 10^{-6}$ s⁻¹, compares with that for $k_1 = 1.8 \times 10^{-4}$ s⁻¹, and leads to a value of $K = \sim70$.

(31) In a recent publication,[21] Hayase, Hrovat, and Borden calculate by B3LYP values for the forward (and reverse) rearrangements of 1,5-diphenyl-1,3-(*Z*)-pentadiene of $\Delta H^{\ddagger} = 32.6$ kcal mol⁻¹. This value, offered without assessment of probable uncertainties, is higher by +3.4 kcal mol⁻¹ than our experimental value. It seems unlikely that the discrepancy can be attributed to the perturbation by *p*-methyl of one of the two phenyl groups.
(32) Van-Catledge, F. A.; Boerth, D. W.; Kao, J. *J. Org. Chem.* **1982**, *47*, 4096−4106.
(33) Kabalka, G. W.; Mohammadi, M.; Hylarides, M.; Finn, R. D. *Org. Prep. Prod. Int.* **1984**, *16*, 321−328.

Table 3. Specific Rate Constants for the Thermal Rearrangement of (*Z*)-2-Ethylidene-1-methylene-1,2,3,4-tetrahydronaphthalene (**10**) to 4-Methyl-3-vinyl-1,2-dihydronaphthalene (**11**)

temp, °C	$(k_1 + k_{-1})^{a,b}$	$(k_1 + k_{-1})^{a,c}$	temp, °C	$(k_1 + k_{-1})^{a,b}$	$(k_1 + k_{-1})^{a,c}$
98.3	2.37	2.44	140.8	95.5	99.3
98.3	2.58	2.27	140.8	97.3	98.8
98.3	2.41	2.35	140.8	96.1	118.0

Arrhenius Parameters
$E_a^d = 26.40 \pm 0.19\ (\pm 0.52)^f$ kcal mol^{-1}; log $A^b = 9.92 \pm 0.10\ (\pm 0.29)^f$
$E_a^e = 27.00 \pm 0.15\ (\pm 0.42)^f$ kcal mol^{-1}; log $A^c = 10.26 \pm 0.09\ (\pm 0.29)^f$
$\Delta H^\ddagger = 26.2 \pm 0.2$ kcal mol^{-1}; $\Delta S^\ddagger = -15.5 \pm 0.5$ eu.

$^a (k_1 + k_{-1}) \times 10^{-6}$ sec^{-1}. ^{b} "Best fit" by allowing each x_e to float in $[(k_1 + k_{-1}) = \ln[(x_e - x_o)/(x_e - x_t)]/t$. ^{c} Using the mean value of 0.988 for x_e from "best fit". ^{d} Based on the "best fit" values for $(k_1 + k_{-1})^b$. ^{e} Based on the "mean value" values for $(k_1 + k_{-1})^c$. ^{f} Error limits at the 95% confidence level.

Compound **10** is prepared from a precursor, (*E*)-2-ethylidene-3,4-dihydro-2*H*-naphthalene-1-one, itself available from α-tetralone and acetaldehyde following a procedure of Riahi et al..[35a] Agreement with the reported NMR spectrum in CDCl$_3$ is good. Irradiation of this ketone generates a photostationary mixture of the desired (*Z*) isomer and the undesired (*E*) isomer. Conversion of (*Z*)-2-ethylidene-3,4-dihydro-2*H*-naphthalene-1-one to **10** is effected by the more reliable method of Petasis and Bwozej,[36] employing dimethyltitanocene, the conventional Wittig procedure having proved unsatisfactory.

Rates of reaction of **10** are determined in three independent runs each at 98.3 and at 140.8 °C (Table 3; Table SI-4 contains the unrefined data). Calculations based on the equation for reversible first-order reactions are carried out by varying values of the concentration of product at equilibrium, x_e, to achieve a best fit of the rate constant. This method leads to $E_a = 26.40 \pm 0.19\ (\pm 1.03\ [95\%\ \text{confidence level}])$ and log $A = 9.92 \pm 0.10\ (\pm 0.57\ [95\%])$. The mean of the "best fit" values, $x_e = 0.9880$ corresponding to $K = 82$, is then used to recalculate specific rate constants. This variant leads to $E_a = 27.00 \pm 0.15\ (\pm 0.85\ [95\%])$ and log $A = 10.26 \pm 0.10\ (\pm 0.58\ [95\%])$.

Preparation of **13** begins with β-tetralone and acetaldehyde to provide a mixture of (*E*)- and (*Z*)-1-ethylidene-3,4-dihydro-1*H*-naphthalene-2-one, which is separated by flash chromatography.[37] The (*E*) isomer is converted to (*E*)-**13** by treatment with dimethyltitanocene.

Rates of reaction of **13** are determined similarly in four independent runs each at 98.4 and at 140.8 °C (Table 4; Table SI-5 contains the unrefined data). In calculations based on the equation for reversible first-order reactions, values of the equilibrium concentration of product (x_e) are varied to achieve best fits of the eight rate constants and lead to $E_a = 26.85 \pm 0.21\ (\pm 0.59\ [95\%\ \text{confidence level}])$ and log $A = 10.07 \pm 0.13\ (\pm 0.33\ [95\%])$. The mean of the "best fit" values of x_e (0.9462 at 98.4 °C and 0.94055 at 140.8 °C, corresponding to $K = 17.6$ and 15.8, respectively) are then used to recalculate specific rate constants. Therefrom Arrhenius parameters for k_1

(34) The specific rate constant at 131.7 °C is omitted from the calculation because its inclusion increases the standard error by more than a factor of 3.
(35) (a) Riahi, A.; Thorey, C.; Hénin, F.; Muzart, J. *Synth. Commun.* **1998**, *28*, 4339−4344. (b) Negishi, E.; Copéret, C.; Ma, S.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5904−5918. (c) Enders, D.; Zhu, J.; Kramps, L. *Liebigs Ann./Recueil* **1997**, 1101−1113.
(36) Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392−6394.
(37) Kinder, F. R., Jr.; Chen, C.-P.; Bair, K. W. *Synth. Commun.* **1997**, *27*, 871−881.

Table 4. Specific Rate Constants for the Thermal Rearrangement of (*E*)-1-Ethylidene-2-methylene-1,2,3,4-tetrahydronaphthalene (**13**) to 3-Methyl-4-vinyl-1,2-dihydronaphthalene (**14**)

temp, °C	$k_1^{a,b}$	$k_1^{a,c}$	temp, °C	$k_1^{a,b}$	$k_1^{a,d}$
98.4	1.88	1.93	140.8	75.6	84.1
98.4	1.77	1.65	140.8	78.6	73.4
98.4	2.06	1.93	140.8	79.2	87.1
98.4	1.85	1.89	140.8	79.3	82.6

Arrhenius Parameters
$E_a^b = 26.85 \pm 0.21\ (\pm 0.59)^e$ kcal mol^{-1}; log $A^b = 10.07 \pm 0.13\ (\pm 0.33)^e$
$E_a^c = 27.15 \pm 0.09\ (\pm 0.23)^e$ kcal mol^{-1}; log $A^c = 10.21 \pm 0.05\ (\pm 0.13)^e$
$\Delta H^\ddagger = 26.4 \pm 0.1$ kcal mol^{-1}; $\Delta S^\ddagger = -15.7 \pm 0.3$ eu.

$^a k_1 \times 10^{-6}$ sec^{-1}. ^{b} "Best fit" by allowing x_e to float in $[(k_1 + k_{-1}) = (1/t)/\ln[(x_e - x_o)/(x_e - x_t)]$. ^{c} Using the mean value of 0.9462 for x_e. ^{d} Using the mean value of 0.945 05 for x_e. ^{e} Error limits at the 95% confidence level.

are calculated: $E_a = 27.15 \pm 0.09\ (\pm 0.23\ [95\%])$ and log $A = 10.21 \pm 0.05\ (\pm 0.13\ [95\%])$.

Discussion

The activation energy of the rearrangement of 1-phenyl-5-*p*-tolylpenta-1(*E*),3(*Z*)-diene [(**E,Z**)-**5**] is 30.1 kcal mol^{-1} or 6.0 kcal mol^{-1} below the uncorrected value (36.1 kcal mol^{-1}) for the paradigm, penta-1,3(*Z*)-diene. Corrections for the difference between *s-trans* and *s-cis* conformations, both $\Delta SE \sim 3.5$ kcal mol^{-1}, leave the estimated energy of activation of the rearrangement-competent *s-cis* conformation unchanged at ~ 6 kcal mol^{-1}. Inclusion of the conjugative interaction of the phenyl group at the 1-position lowers the energy of activation by ~ 5.1 kcal mol^{-1} for a total of ~ 11 kcal mol^{-1}. However, the phenyl group at the 5-position very likely introduces an opposing, rate-accelerating effect of equal or comparable magnitude as it becomes involved in the transition region. It is not clear how a correction for conjugative interaction is to be incorporated in a credible way. Hayase, Hrovat, and Borden have calculated enthalpies of activation for the fully degenerate 1(*E*),5-diphenyl-1,3(*Z*)-pentadiene of 32.6 kcal mol^{-1} from its *s-trans* conformation and 28.8 kcal mol^{-1} from its *s-cis* conformation.[21] Conjugative interaction of phenyl in the educts and steric factors are implicit in these DFT calculations. Vis-à-vis their calculated value of $\Delta H^\ddagger$ for the paradigm (32.0 kcal mol^{-1}), the lowering is 3.2 kcal mol^{-1}. The apparent discrepancy of 2.8 kcal mol^{-1} with the experimentally based value may seem large (6−3.2 kcal mol^{-1}), but taking realistic account of the uncertainties in the experimental value, and the inaccuracies in the DFT-calculated value and the MM-2-calculated conformational correction, we consider the agreement satisfactory![31]

Recognition of the hybrid relation of the transition region of the 1,5-hydrogen shift to Cope's rearrangement and the dyotropic shift of two hydrogen atoms[38] provides models for the paltry size of the stabilization energies accruing from perturbation by phenyl (Charts 1 and 2). A model for the intramolecular 1,5-hydrogen shift more realistic than a simplistic dissociation into a pentadienyl radical and an hydrogen atom can be constructed from the extensively investigated, intermolecular methane/methyl radical transfer. Starting from the known heat

(38) (a) Doering, W. v. E.; Rosenthal, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 4534. (b) Grimme, W.; Pohl, V.; Wortmann, J.; Frowein, D. *Liebigs Ann.* **1996**, 1905−1916. (c) Corey, E. J.; Pasto, D. J.; Mock, W. L. *J. Am. Chem. Soc.* **1961**, *83*, 2957−2958. (d) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682−708. (e) Houk, K. N.; Li, Y.; McAllister, M. A.; O'Doherty, G.; Paquette, L. A.; Siebrand, W.; Smedarchina, Z. K. *J. Am. Chem. Soc.* **1994**, *116*, 10895−10914.

Chart 1
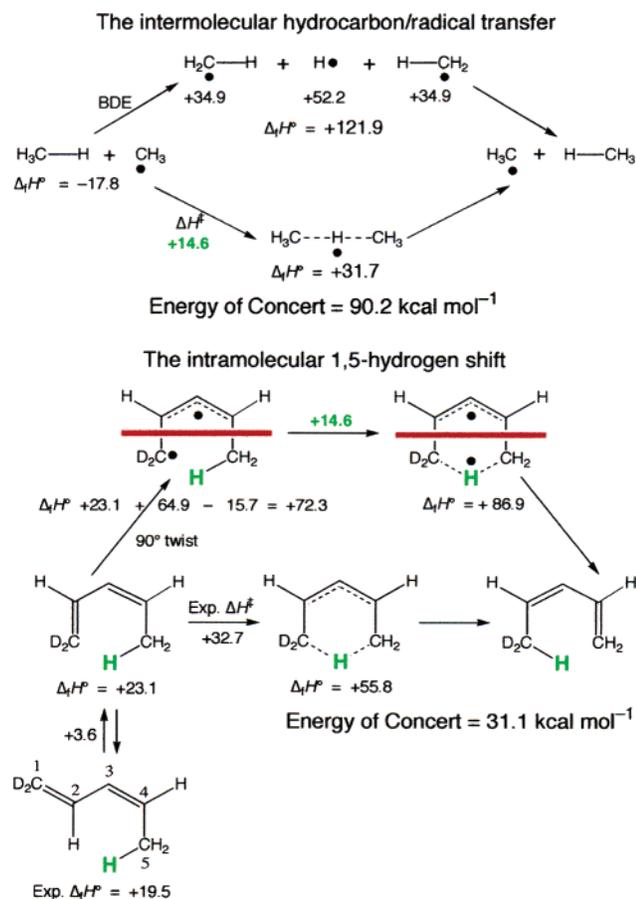
Chart 2

of formation of *s-trans cis*-piperylene ($+19.5$ kcal mol^{-1})[39] and the credible difference of the *s-cis* conformation ($+3.6$ kcal mol^{-1}), proceeding to the interposition of an interaction-blocking barrier (the red line in the lower part of Chart 1) by a 90° twist about the C1−C2 terminal double bond ($+64.9$ kcal mol^{-1}),[40] introducing the energy of allylic stabilization (-15.7 kcal mol^{-1}),[41] and adding the energy of activation of the methane/methyl-radical hydrogen transfer ($+14.6$ kcal mol^{-1})[7] lead to an estimated energy of concert of 31.1 kcal mol^{-1}. Theoretical calculations of the intermolecular transfer have uniformly found a 180°, linear transition structure to be the energy minimum. By contrast, the optimum structures of the cyclic transition regions in the 1,5-hydrogen shifts of pentadienes and the dyotropic transfer are bent and likely higher in energy than the linear optimum.[42,43] The energy of concert may well be a lower estimate.

As calibration for perturbation by phenyl, note the claimed energies of activation for the toluene/methyl-radical hydrogen transfer (9.5 kcal mol^{-1}), the methane/benzyl-radical hydrogen
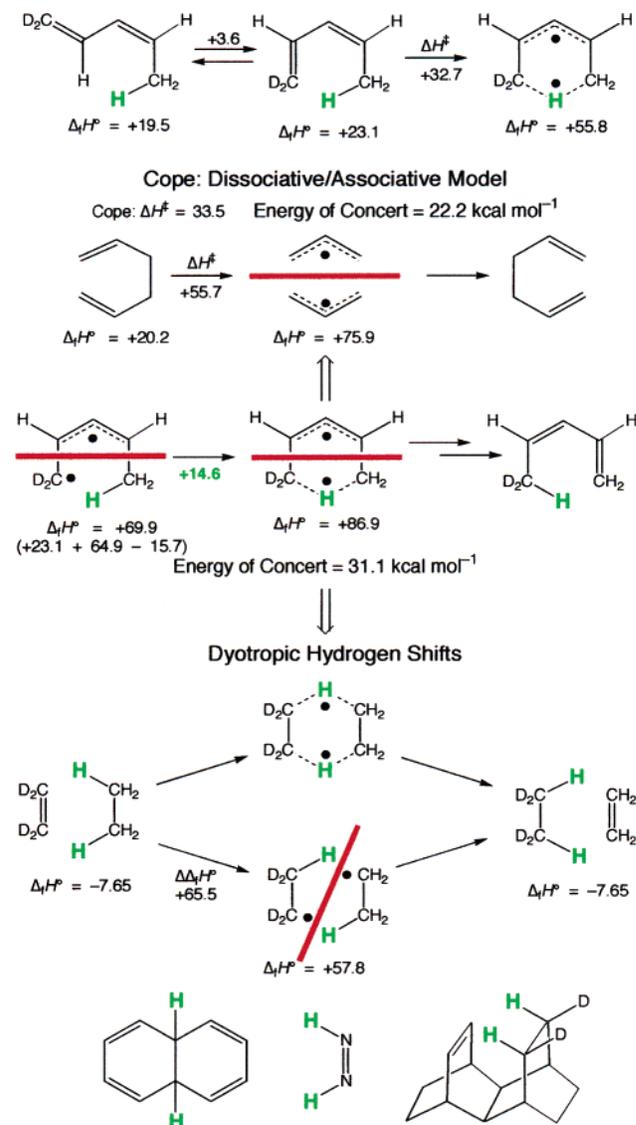
transfer (25.9 kcal mol^{-1}), and the most apposite, toluene/benzyl-radical hydrogen transfer (15.8 kcal mol^{-1}).[44] The latter is so close to the $+14.6$ kcal mol^{-1} of the methane/methyl-radical hydrogen transfer that the small effect observed in **5** is more easily understandable. Consistently, a *symmetrical* perturbation by two phenyl groups has little effect on the transition region.

Compounds **10** and **13** are so constructed as to need no thermochemical corrections for the *s-trans/s-cis* conformational factor. Simultaneously the fused benzene groups are no longer ad libitum but are more nearly coplanar with the pentadienyl system. Their capacity for π-electronic interaction may thereby be enhanced but at the expense of a flexibility concordant with the minimization of adventitious steric interactions.

The parent **7** has an energy of activation of 30.6 kcal mol^{-1}, which is lower by 2.1 kcal mol^{-1} than the 32.7 kcal mol^{-1} of the *s-trans/s-cis*-corrected value being taken for the *s-cis*, unsubstituted paradigm (Figure 3). No explanation for the discrepancy is immediately apparent, beyond the already

(39) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.
(40) Doering, W. v. E.; Roth, W. R.; Bauer, F.; Breuckmann, R.; Ebbrecht, T.; Herbold, M.; Schmidt, R.; Lennartz, H.-W.; Lenoir, D.; Boese, R. *Chem. Ber.* **1989**, *122*, 1263−1275.
(41) Korth, H. G.; Trill, R.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483−4489.
(42) In this connection, regard the much lower energy of activation ($E_a = 21.5$ kcal mol^{-1}; Roth, W. R *Tetrahedron Lett.* **1964**, 1009) reported by Baldwin and Reddy for the 1,7-hydrogen shift in hepta-1,(Z)3(Z)5-triene. Although the comparison of the antarafacial, helical eight-membered transition region with the suprafacial, planar six-membered 1,5-hydrogen shift is problematic in several ways, the crucial, core element has essentially become linear.
(43) Baldwin, J. E.; Reddy, V. P. *J. Am. Chem. Soc.* **1988**, *110*, 8223−8228.

(44) Like Ma and Schobert,[7a] we are not engaging in assessment of the accuracy of these values.

mentioned high uncertainty in the experimental value taken for the paradigm. The experimental activation energy for the 2-benzo analogue **10** is 27.0 kcal mol^{-1} or 3.6 kcal mol^{-1} below **7**. A similar analysis of the 3-benzo analogue **13**, $E_a = 27.2$ kcal mol^{-1}, reveals a comparable lowering of 3.4 kcal mol^{-1}.

The enthalpies of activation parameters from **10** and **13** may also be corrected for conjugative interaction in the educt by transferring values reported for similarly benzo-fused analogues. Conjugative interaction of the more nearly coplanar benzo group with a C−C double bond appears to be increased by ∼0.7 kcal mol^{-1}.[45] This value, if added to the correction of 2.5 kcal mol^{-1} applied above to 2-phenyl-1,3(Z)-pentadiene, would increase the estimated correction to 3.2 kcal mol^{-1}.

The observed activation energy for **10**, corrected by this value, becomes 23.8 kcal mol^{-1}, implying a stabilization in the transition region of 6.8 kcal mol^{-1}. A similar analysis of the 3-benzo analogue **13** leads to an apparent stabilization of 6.6 kcal mol^{-1}. By way of calibration, the experimental activation energy for the thermal cis−trans isomerization of a benzo-fused 1,6-diphenylhexa-1,3,5-triene is 7.2 kcal mol^{-1} lower than a comparable hexa-1,3,5-triene as model; that is, each phenyl has lowered the energy of activation by 3.6 kcal mol^{-1}.

Hayase, Hrovat, and Borden have very recently calculated values of the enthalpies of activation by the DFT procedure, BLYP/6-31G*, for the *s-cis* series, **7**, **10**, and **13**.[46]

Their calculated values for $\Delta H^{\ddagger}$ are 33.5, 29.7, and 29.7, respectively. Comparisons with the corresponding experimental values of E_a, 30.6, 27.0, and 27.2 kcal mol^{-1}, respectively, are uniformly higher by ∼2.5 kcal mol^{-1}, a discrepancy that exceeds in our judgment plausible uncertainties in the experimental values. The calculated *differences* between **7** and **10** and **7** and **13** are, however, both −3.8 kcal mol^{-1}, in fine agreement with the experimental differences of −3.6 and −3.2 kcal mol^{-1}, respectively. Hayase, Hrovat, and Borden ascribe these differences to relief of a greater strain in the educts on passing to the transition structures.

Several suggestions, some being pursued at present, that may lead to further insight into the nature of the transition region (Chart 3) are offered. The introduction of sufficient rigidity into the 1,5-diphenyl system by way of compound **16** achieves a minimal goal of removing the *s-trans/s-cis* correction. Comparison of the activation parameters for compounds **17** and **18** may help unravel the contribution to the transition region of conjugative interaction in the educt. In respect of 2-phenyl derivatives, advantage can be taken of the possibility of introducing *two* phenyl groups at the same type of position. The resulting degenerate 2,4-diphenyl derivative, compound **19**, is in every way comparable to the 1,5-diphenyl derivative already examined in this work, while the more rigid compound **20** removes the *s-trans/s-cis* conformational factor and confines both phenyl groups to near coplanarity without appearing to place significant steric restrictions on the hydrogen atoms of the 1,5-carbon atoms at the core of the hydrogen shift. As the basis of a further assessment of the effect of a phenyl group in the 3-position, compound **21** in conjunction with compound **22** may be helpful. Compound **23** bears on the interesting question

(45) Doering, W. v. E.; Benkhoff, J.; Shao, L.-m. *J. Am. Chem. Soc.* **1999**, *121*, 962−968.
(46) Hayase, S.; Hrovat, D. A.; Borden, W. T. Unpublished results (with permission to quote).

Chart 3
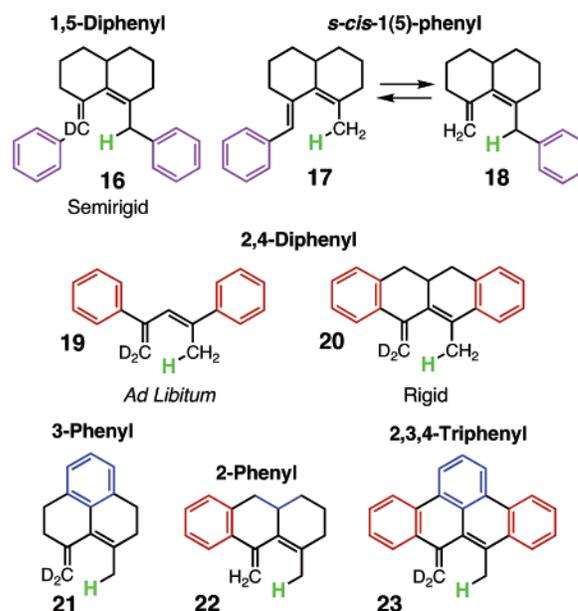
of additivity versus competition between phenyl groups at opposite ends of the continuum.

Conclusions

The *s-cis*-locked compounds **10** and **13** of Figure 9 have revealed energies of activation lowered essentially identically by 3.6 and 3.4 kcal mol^{-1}, respectively, regardless whether the benzo group is positioned at C2 or C3. The small magnitude of the stabilizations is in accord with the equally small size of the difference between the stabilization energies of allyl and cinnamyl radicals. Although other explanations can be entertained, these stabilizations are consistent with the hypothesis of a chameleon-like transition region that responds to a demand for π-electron delocalization by substitution at the 2-position by moving toward the allylic end of the continuum and to substitution at the 3-position by moving toward the pentadienyl end (Figure 2). Unlike in the Cope rearrangement where a large change in geometry is involved (Figure 1), in the 1,5-hydrogen shift change in geometry is negligible. Regardless of explanation, it has been credibly established that radical-stabilizing phenyl groups lower the energies of activation at all three types of position in the transition region of the 1,5-hydrogen shifts in acyclic 1,3(Z)-pentadienes.

Experimental Section

General Procedures. ^{1}H (500 MHz) and ^{13}C (125.7 MHz) NMR spectra were measured in benzene-d_6, unless otherwise noted, on a Varian Unity/Inova 55 Instrument. Chemical shifts are reported in ppm (δ) with respect to residual C$_6$D$_5$H (7.15 ppm for ^{1}H and 128.0 ppm for ^{13}C). Spin−lattice relaxation times (T_1) were determined by the inversion−recovery method in benzene-d_6. Preparative GC on a Varian Aerograph A90-P3 instrument employed a 3-m column of 20% Carbowax 20M on Anachrom AS with He as a carrier gas. Analytical gas chromatography was conducted on a Hewlett-Packard (HP) 5890A gas chromatograph equipped with a J&W Scientific, Inc. DB-225 (0.53 mm i.d. × 30-m, 1 μm film thickness) megabore column and an HP 3393A integrator.

Triphenyl-β-p-tolylethylphosphonium Bromide. To a suspension of methyltriphenylphosphonium bromide (6.12 g, 17 mmol) in 60 mL

of anhydrous tetrahydrofuran (THF) in a 100-mL, round-bottomed flask under argon, 8.5 mL of a solution of *n*-butyllithium (2.0 M in pentane) were added at 0 °C. After the mixture was warmed to room temperature, stirred for 30 min, and recooled to 0 °C, a solution of *p*-tolylmethyl bromide (1.57 g, 8.5 mmol) in anhydrous THF (5 mL) was added by syringe over a 10-min period. After the mixture was stirred for 2 h at 0 °C and overnight at 25 °C, absolute ethanol was added dropwise until no further solid precipitated. The filtered precipitate was washed 3 times with THF, dispersed in 6 mL of water, filtered, washed with 1 mL of water, and dried over phosphorus pentoxide to give 2.1 g (53%) of a colorless solid: ¹H NMR (CDCl₃) 2.23 (s, 3H), 2.95−3.02 (m, 2H), 3.96−4.02 (m. 2H), 7.00 (d, J = 8.05 Hz, 2H), 7.12 (d, J = 8.05 Hz, 2H), 7.65−7.85 (m. 15H).

(*E,Z*)- and (*E,E*)-1-Phenyl-5-*p*-tolylpenta-1,3-diene [(*E,Z*)-5 and (*E,E*)-5]. Triphenyl-*β*-*p*-tolylethylphosphonium bromide (1.82 g, 3.95 mmol) was converted to its Wittig reagent as above. A solution of *trans*-cinnamaldehyde (0.52 g, 3.95 mmol) in anhydrous THF (5 mL) was added at 0 °C by syringe over a period of 20 min. After concentration in a vacuum, the mixture was treated with 20 mL of water and extracted twice with pentane (30 mL each). The combined extracts were washed with water (40 mL) and brine, dried over Na₂SO₄, filtered, concentrated, and subjected to column chromatography (neutral alumina, hexane) to give a mixture of (*E,Z*)-5 (67%) and (*E,E*)-5 (33%) as a colorless oil (66%). ¹H NMR (*E,Z*)-5: 2.12 (s, 3H), 3.47 (d, J = 7.81 Hz, 2H), 5.60−5.65 (m, 1H), 6.19−6.24 (m, 1H), 6.49 (d, J = 15.63 Hz, 1H), 6.97−7.27 (m, 10H). ¹H NMR (*E,E*)-5: 2.14 (s, 3H), 3.29 (d, J_1 = 6.84 Hz, 2H), 5.77−5.83 (m, 1H), 6.11−6.16 (m, 1H), 6.34 (d, J = 15.63 Hz, 1H), 6.70 (dd, J_1 = 15.63 Hz, J_2 = 10.74 Hz, 1H), 6.91−7.27 (m, 9H).

(*E,Z*)- and (*E,E*)-5-Phenyl-1-*p*-tolylpenta-1,3-diene (*E,Z*)-6 and (*E,E*)-6. The conversion of triphenyl-*β*-phenylethylphosphonium bromide (1.00 g, 2.2 mmol) and 4′-methylcinnamaldehyde (0.32 g) to a mixture (0.35 g) of (*E,Z*)-6 (70%) and (*E,E*)-6 (30%) was effected by the procedure above: ¹H NMR (*E,Z*)-6: 2.09 (s, 3H), 3.46 (d, J = 7.81 Hz, 2H), 5.55−5.60 (m, 1H), 6.22−6.26 (m, 1H), 6.53 (d, J = 15.63 Hz, 1H), 6.95−6.97 (m, 2H), 7.06−7.25 (m, 8H); (*E,E*)-6 2.09 (s, 3H), 3.27 (d, J_1 = 6.84 Hz, 2H), 5.72−5.78 (m, 1H), 6.11−6.16 (m, 1H), 6.38 (d, J = 15.63 Hz, 1H), 6.67−6.72 (m, 1H), 6.95−6.97 (m, 2H), 7.04−7.22 (m. 7H).

Kinetics. The sample (2−3 mg) in 0.2 mL of (benzene-*d*₆) in an NMR tube was degassed through three freeze−thaw cycles and sealed under vacuum. The sealed tube was then heated in the vapors of boiling solvents for the specified periods of time (data given in the Supporting Information, Table SI-2): anisole, bp 153.6−153.8; diethyl oxalate, bp 185.1−185.4.

(*E*)-2-Ethylidenecyclohexan-1-one. In a 250-mL, two-necked, round-bottomed flask fitted with a 30-mL, pressure-equalizing addition funnel, sodium ethoxide (430 mg, 6.4 mmol) was added to cyclohexanone (13.2 mL, 128 mmol), cooled to 0 °C, and stirred for 15 min, at which time a solution of acetaldehyde (14.3 mL, 255 mmol) and cyclohexanone (13.2 mL, 128 mmol) was added from the addition funnel dropwise over 2 h. After being stirred at 0 °C for 1 h, the reaction mixture was quenched with water (3 mL), transferred to a separatory funnel, and treated with oxalic acid (0.21 g, 1.6 mmol) dissolved in water (3 mL). After being washed with brine (2 × 20 mL), the organic solution was distilled under reduced pressure, first at 95 °C and 95 mmHg to remove residual water and cyclohexanone, then at 110 °C and 5 mmHg to afford 3.3 g of (*E*)-2-ethylidenecyclohexan-1-one in 21.9% of theoretical yield: ¹H NMR 1.24 (m, 2H); 1.32 (m, 5H); 2.03 (m, 2H); 2.19 (t, J = 6.59 Hz, 2H); 6.86 (m, 1H); ¹³C NMR 13.07, 23.38, 23.60, 26.35, 40.16, 133.16, 137.17, 198.03.

Irradiation of (*E*)-2-Ethylidenecyclohexan-1-one. In a 500-mL, single-necked, round-bottomed flask, a sample of ketone (7.24 g, 58 mmol) in benzene (450 mL) was degassed by passing through it a stream of nitrogen for 20 min. The flask was then fitted with a reflux condenser and irradiated with a Hanovia 450-W, medium-pressure

mercury lamp for 10 h. GC analysis (50 °C for 15 min, 15 °C per min to 200 °C, and finally 15 min isothermal) showed two major peaks: starting material at 23.08 min and a new peak at 21.36 min in a ratio of 1 to 0.9.

(*Z*)- and (*E*)-2-Ethylidene-1-methylenecyclohexane (*Z*)-7 and (*E*)-7. In a 500-mL, four-necked, round-bottomed flask fitted with a 150-mL, pressure-equalizing addition funnel, methyltriphenylphosphonium bromide (17.6 g, 0.05 mol) was suspended in tetrahydrofuran (THF) (150 mL, freshly distilled from sodium and benzophenone) under an argon atmosphere. *n*-Butyllithium (24.5 mL, 2.0 M solution in pentane) was added at −78 °C (became red/orange). The resulting Wittig reagent was warmed to room temperature, stirred for 30 min, then cooled to −78 °C. A solution of the 1:0.9 mixture of enones (6.1 g, 0.05 mol) in THF (60 mL) was added with stirring over 1 h. After an additional hour of being stirred, the reaction mixture was diluted with water (200 mL) and separated into an organic layer and an aqueous layer, which was extracted with pentane (2 × 40 mL). The combined organic solutions were washed with water (4 × 200 mL), dried over Na₂SO₄, vacuum filtered, and concentrated by distillation. Distillation at reduced pressure gave 2.66 g of a clear oil consisting of 30% of (*Z*)-7 and 39% of (*E*)-7 by analytical GC. Preparative GC at 72 °C provided pure samples. (*Z*)-7: ¹H NMR 1.46−1.54 (m, 4H), 1.72 (dt, J = 0.98 Hz, 6.84 Hz, 3H), 2.12−2.17 (m, 4H), 4.77 (d, J = 2.93 Hz, 1H), 4.99 (t, J = 0.98 Hz, 1H), 5.27 (q, J = 6.84 Hz, 1H); ¹³C NMR 14.48, 28.04, 28.39, 37.13, 38.28, 110.68, 118.15, 141.03, 146.81. (*E*)-7: 1.41 (m, 2H), 1.47 (m, 2H). 1.52 (d, J = 6.84 Hz, 3H), 2.18 (m, 4H), 4.66 (d, J = 0.98 Hz, 1H), 4.98 (d, J = 1.95 Hz, 1H), 5.64 (q, J = 6.84 Hz, 1H); ¹³C NMR 13.05, 26.45, 27.50, 28.38, 35.82, 107.39, 117.49, 141.08, 151.51 (the missing ¹³C(C-sp²) resonance is presumed to be hidden under the solvent).

Heating (*Z*)-2-Ethylidene-1-methylenecyclohexane, (*Z*)-7. Samples of (*Z*)-7 (7 mg, 7.5 mmol) in 0.7 mL of benzene-*d*₆ in a lead-potash glass tube were degassed through three freeze−thaw cycles and sealed under vacuum. The tubes were heated in the vapors of the following boiling solvents: *n*-butyl alcohol (117.4−118.3 °C), tetrachloroethylene (121.3−121.8 °C), chlorobenzene (131.3−132.0 °C), mesitylene (164.9−165.2 °C), *p*-methylanisole (175.5−175.9 °C), and diethyloxalate (185.5−186.0 °C). For analysis, the tubes were opened. The contents were transferred to NMR tubes and analyzed quantitatively by the absorption at 5.27 and 4.77 for (*Z*)-7 and those at 6.89 and 5.15 ppm for **8**. A sample of the product, 1-methyl-2-vinylcyclohexene (**8**) was isolated from the combined reaction products of the various kinetic runs by preparative GC using a 3-m, 20% Carbowax 20M on Anakrom column at 72 °C: ¹H NMR 1.41−1.45 (m, 2H), 1.48−1.51 (m, 2H), 1.61 (s, 3H), 1.83−1.87 (m, 2H), 2.09−2.12 (m, 2H), 4.99 (d, J = 10.99 Hz, 1H), 5.15 (d, J = 17.34 Hz, 1H), 6.89 (dd, J = 17.34, 10.99 Hz, 1H); ¹³C NMR 19.15, 23.05, 23.16, 25.07, 33.00, 110.10, 133.10, 135.53.

(*Z*)-2-Ethylidene-3,4-dihydro-2*H*-naphthalene-1-one. Following the general procedure of Riahi et al.,[35a] α-tetralone (6.0 g, 0.04 mol) and acetaldehyde (1.8 g, 0.04 mol) are condensed to yield 5.7 g of crude product, which, after flash-chromatography (22 × 3.5 cm² column of silica gel, 14:1 petroleum ether/ethyl acetate), affords 2.8 g of (*E*)-2-ethylidene-3,4-dihydro-2*H*-naphthalene-1-one (2.4 g after evaporative distillation, mp 38 °C (lit. 38 °C[35b])): ¹H NMR[35b,c] (benzene-*d*₆) 1.38 (d of t, J = 6.84, 1.47 Hz, 3H), 2.29 (br t, J = 6.35 Hz, 2H), 2.42 (t, J = 6.35 Hz, 2H), 6.82 (d, J = 7.33 Hz, 1H), 7.01 (t of d, J = 7.81, 0.98 Hz, 1H), 7.06 (t of d, J = 7.32, 1.95 Hz, 1H), 8.42 (dd, J = 7.81, 1.47 Hz, 1H) (one H is hidden under the H of the solvent benzene-*d*₆); ¹H NMR (CDCl₃) 1.88 (d, J = 7.32, Hz, 3H), 2.79 (br t, J = 6.35 Hz, 2H), 2.95 (t, J = 6.84 Hz, 2H), 7.03 (q of d, J = 5.37, 1.47 Hz, 1H), 7.25 (t, J = 6.35 Hz, 1H), 7.33 (t, J = 7.33 Hz, 1H), 7.46 (t of d, J = 7.33, 1.47 Hz, 1H), 8.09 (dd, J = 6.84, 0.98 Hz, 1H); ¹³C NMR (benzene-*d*₆) 14.10, 25.81, 29.54, 127.72, 128.89, 129.13, 133.30, 134.56, 134.93, 136.63, 144.21, 186.69.

An X-ray crystallographic determination confirms the assigned structure and affords a torsional angle of −7.8 ° between the carbonyl group and the double bond.[47]

Following the procedure of Riahi et al.,[35a] a solution of the ketone (7.25 g, 0.04 mol) in 350 mL of benzene in a 500-mL, three-necked Pyrex flask was degassed by a stream of nitrogen for 20 min and then irradiated for 19 h with a Hanovia 450-watt medium-pressure mercury lamp with stirring. After concentration, the resulting oil (7.22 g, *E/Z* ratio 1:1 by NMR) was flash-chromatographed as above to yield 1.2 g of (*Z*)-2-ethylidene-3,4-dihydro-2*H*-naphthalene-1-one (>99% of purity): ^{1}H NMR 2.16 (d of t, *J* = 7.32, 1.47 Hz, 3H), 2.26 (t of t, *J* = 6.35, 1.46 Hz, 2H), 2.48 (t, *J* = 6.35 Hz, 2H), 5.66 (q of t, *J* = 7.32, 1.47 Hz, 1H), 6.80 (d, *J* = 7.33 Hz, 1H), 7.00 (t, *J* = 7.06 Hz, 1H), 7.05 (t of d, *J* = 7.33, 1.47 Hz, 1H), 8.40 (d, *J* = 7.81 Hz, 1H).

(*Z*)-2-Ethylidene-1-methylene-1,2,3,4-tetrahydronaphthalene (10). Following a general procedure of Petasis and Bzowej,[36] a solution of the ketone above (1.4 g, 9 mmol) in toluene (5 mL) added to a solution of bis(cyclopentadienyl)dimethyltitanium (5.6 g, 27 mmol) in toluene (62 mL) was stirred for 24 h at 65 °C, diluted with petroleum ether (70 mL) at room temperature, and filtered from separated titanium salts. The filtrate was concentrated to an oil, which was flash-chromatographed (20 × 6.5 cm, neutral alumina, 14:1 petroleum ether/ethyl acetate) to give (*Z*)-2-ethylidene-1-methylene-1,2,3,4-tetrahydronaphthalene (195 mg after evaporative distillation): ^{1}H NMR 1.77 (d, *J* = 7.08 Hz, 3H), 2.34 (t, *J* = 6.59 Hz, 2H), 2.68 (t, *J* = 6.59 Hz, 2H), 5.08 (d, *J* = 0.73 Hz, 1H), 5.39 (t (q?), *J* = 7.00 Hz, 1H), 5.77 (s, 1H), 6.89 (m, 1H), 7.03 (m, 2H), 7.61 (m, 1H).

Kinetic studies were effected in the manner described above for **7**, using resonances at 5.77 ppm for (**Z**)**-10** and 5.19 for **11**. From samples that had reached equilibrium, the spectrum of the product, 4-methyl-3-vinyl-1,2-dihydronaphthalene (**11**), was obtained: ^{1}H NMR 1.96 (d, *J* = 2.93 Hz, 3H), 2.27 (t of d, *J* = 7.93, 1.47 Hz, 2H), 2.55 (t, *J* = 8.30 Hz, 2H), 5.10 (d, *J* = 10.99 Hz, 1H), 5.19 (dd, *J* = 17.09, 0.98 Hz, 1H), 6.96 (m, 2H), 7.05 (t of d, *J* = 7.32, 1.22 Hz, 1H), 7.11 (t of d, *J* = 7.45, 1.47 Hz, 1H), 7.20 (d, *J* = 7.57 Hz, 1H).

(*E*)-1-Ethylidene-2-methylene-1,2,3,4-tetrahydronaphthalene (13). Following a procedure described in detail using benzaldehyde,[37] *β*-tetralone (10 g) and acetaldehyde (3.8 mL) were condensed to afford 12.5 g of crude product, from which 3.1 g of (*E*)-1-ethylidene-3,4-dihydro-1*H*-naphthalene-2-one and 4.3 g of (*Z*)-1-ethylidene-3,4-dihydro-1*H*-naphthalene-2-one were isolated by flash chromatography (15 × 6.5 cm², silica gel, 14:1 petroleum ether/ethyl acetate), the (*E*) isomer being the first to elute. ^{1}H NMR (*Z*)-isomer: 2.09 (d, *J* = 7.69 Hz, 3H), 2.57 (br t, *J* = 6.59 Hz, 2H), 2.94 (t, *J* = 3.30 Hz, 2H), 7.05 (q, *J* = 7.69 Hz, 1H), 7.25 (m, 3H), 7.38 (d, *J* = 6.59 Hz, 1H). (*E*)-isomer: 2.29 (d, *J* = 7.32 Hz, 3H), 2.62 (br t, *J* = 6.59 Hz, 2H), 2.97 (t, *J* = 6.59 Hz, 2H), 7.56 (q, *J* = 7.32 Hz, 1H), 7.22 (m, 3H), 7.38 (d, *J* = 9.15 Hz, 1H).

Following the same procedure as above, bis(cyclopentadienyl)-dimethyltitanium (6.2 g, 30 mmol) and (*E*)-1-ethylidene-3,4-dihydro-1*H*-naphthalene-2-one (1.7 g, 10 mmol) were allowed to react to afford 1.64 g of dark-brown oil, which was flash-chromatographed over neutral alumina to give, after evaporative distillation, 300 mg of **13**: ^{1}H NMR 1.85 (d, *J* = 7.33 Hz, 3H), 2.33 (t, *J* = 6.84 Hz, 2H), 2.66 (t, *J* = 6.84 Hz, 2H), 4.94 (d, *J* = 1.95 Hz, 1H), 5.03 (dd, *J* = 2.20, 0.98 Hz, 1H), 6.08 (q, *J* = 7.32 Hz, 1H), 6.91 (d, *J* = 8.30 Hz, 1H), 7.04 (m, 2H), 7.46 (d, *J* = 7.81 Hz, 1H).

Kinetic studies were effected in the manner described above for **7**, using resonances at 5.13 ppm for (**E**)**-13** and 6.50 for **14**. From samples that had reached equilibrium, the spectrum of the product, 3-methyl-4-vinyl-1,2-dihydronaphthalene (**14**), was obtained: ^{1}H NMR 1.78 (s, 3H), 1.97 (t, *J* = 7.57 Hz, 2H), 2.51 (t, *J* = 7.57 Hz, 2H), 5.27 (dd, *J* = 17.82, 2.20 Hz, 1H), 5.32 (dd, *J* = 11.35, 2.20 Hz, 1H), 6.74 (m, 1H), 7.07 (m, 1H), 7.29 (m, 2H), 7.43 (d, *J* = 7.81 Hz, 1H).

Supporting Information Available: Untreated data from the kinetic studies summarized in Tables SI-1 through SI-5 and one figure of three additional rearrangements of alkyl-substituted 1,3(*Z*)-pentadienes (eight pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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