Perturbation of Cope's Rearrangement: 1,3,5-Triphenylhexa-l,5-diene. Chameleonic or Centauric Transition Region?

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Abstract: Two types of perturbations of Cope's rearrangement are distinguished by their occupancy of sets of four "active" and two "nodal" positions. A "chameleonic" model of a continuum of chair-like transition regions is defined as extending from two noninteracting allyl radicals at one extreme to cyclohexa-1,4-diyl diradical at the other. Perturbations are analyzed quantitatively in terms of obligatory corrections for conjugative interaction in the educt, and a model of the transition region that specifies transference of stabilization energies of the perturbing substituents on allyl radicals if occupying active positions, and on secondary radicals if occupying nodal positions. When this model is applied to the chameleonic 2,5- (nodal) and 1,4- (active) diphenylhexa-l,5-dienes, good agreement with empirical lowering of enthalpies of activation per phenyl group of −8.7 and −4.4 kcal mol^{-1}, respectively, is obtained. In a perturbation of mixed type, 1,3,5-triphenylhexa-1,5-diene (1,3-diphenyl-active; 5-phenyl-nodal), a novel question is addressed: Will the stronger of the two types alone prevail (transition region remaining chameleonic), or will the stabilizing capacity of both be realized (centauric domain)? The result is close to, but perhaps somewhat shy of, the full additivity expected of the centauric model.

Introduction

Cope's rearrangement of hexa-1,5-dienes[1] is a major, quintessentially *degenerate* reaction, which leaves the seeker after mechanistic insight little scope beyond the fundament of its thermochemistry and response to perturbations. If chemistry is the science of the transformation of one structure of matter into another, its ultimate goal is the quantitative prediction of positions of equilibrium and rates of reaction. The perturbational approach seeks conceptual schemes that permit substitutions on an archetype to be translated into changes in enthalpies and entropies of formation of educt and product, and of the transition region leading to rate-determining intermediates if multistep, or directly to products if single step.[2−4] The goal of the quantum chemical, theoretical approach is the same, but its realization involves de novo independent calculation of heats of atomization of educt and transition structure, their difference then being the enthalpy of activation predicted directly without reference to the archetype, which plays no essential role. These considerations are pictured in Figure 1.
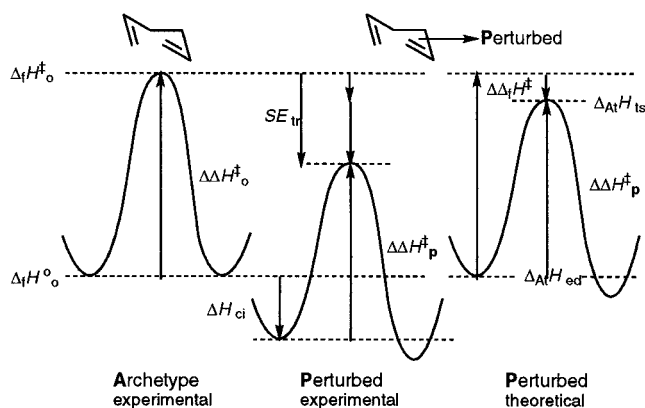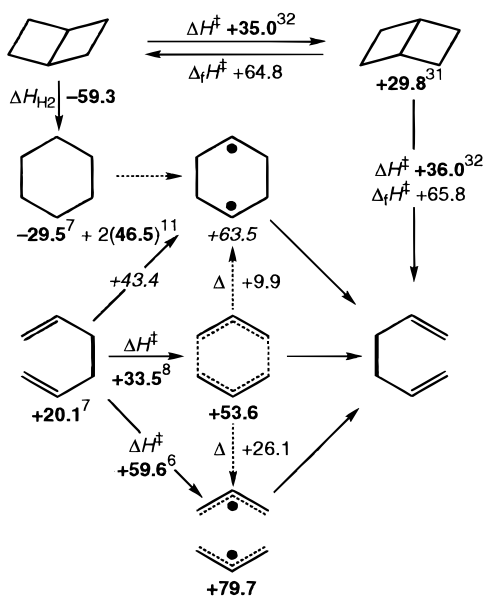

Figure 1. Enthalpies of formation of the educts and transition regions for archetypal hexa-1,5-diene and a perturbed derivative illustrate the relations of conjugative interaction (ΔH_{ci}), differences in enthalpy of activation ($\Delta\Delta_f H^{\ddagger}$), and their sum, stabilization energy in the transition region (SE_{tr}). A comparable depiction of the theoretically calculated perturbed system is included at an arbitrary energy level.

Discussion

Mechanistic Hypotheses. Three models shown in Scheme 1 have been the historic focus of mechanistic attention and continue to be "the usual suspects". At one extreme, as an alternative to the single-step, concerted mechanism, Cope posited dissociation into a pair of noninteracting allyl radicals followed by their random recombination, the homolytic-colligative mechanism, which turned out to be inconsistent with a cross-over experiment.[5] At no subsequent time, during which the empirical enthalpy of formation of the allyl radical fluctuated widely, did this mechanism acquire thermochemical credibility.

(1) See reviews by (a) Rhoads, S. J. In *Molecular Rearrangements*; de Mayo, P., Ed.; Wiley: New York, 1963; Vol. 1, pp 684−696; (b) Gajewski, J. J. *Hydrocarbon Thermal Rearrangements*; Academic: New York, 1981; pp 166−176.

(2) "Whereas it has been adequate to consider *the* mechanism, or *the* transition state, for a reaction, as molecules become more complicated, the bond-breaking process may need to be viewed as a family of individual processes, the number of which increases with the complexity of the empirical formula..."[3] If "transition state" is reserved for individual "state-to-state" transitions and "transition structure" for the "point" resulting from theoretical computations, the entire family of closely related paths encountered in reactions of molecules of many internal degrees of freedom is perhaps better differentiated by "transition region", a term recently introduced by Professor John E. Baldwin[4] (see also Houk et al.[13a]).

(3) Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1974,** *96,* 1168−1187.

(4) Baldwin, J. E. *J. Comput. Chem.* **1998,** *19,* 222−231; Baldwin, J. E.; Bonacorsi, S. J., Jr.; Burrell, R. C. *J. Org. Chem.* **1998,** *63,* 4721−4725.

(5) Cope, A. C.; Hofmann, C. M.; Hardy, E. M. *J. Am. Chem. Soc.* **1941,** *63,* 1852−1857.

Scheme 1

The currently best value for the enthalpy of formation of the allyl radical, $+39.9 \pm 0.7$ kcal mol^{-1},[6] places two allyl radicals 26.1 kcal mol^{-1} above the experimental enthalpy of activation of the archetype, hexa-1,5-diene: $\Delta_f H^0 = +20.1 \pm 0.2$ kcal mol^{-1};[7] $\Delta H^{\ddagger} = 33.5 \pm 0.5$ kcal mol^{-1}; $\Delta S^{\ddagger}$ -13.8 ± 1.0 cal mol^{-1} K^{-1}.[8]

At the other extreme, another two-step model is imagined to generate by covalent bond formation between C-1 and C-6 an intermediate "cyclohexa-1,4-diyl" diradical, which by cleavage either reverts to the original hexa-1,5-diene or proceeds to the product of rearrangement (associative-dissociative mechanism). This hypothetical "diradical" is strictly defined as cyclohexane from which hydrons have been removed from the 1 and 4 positions at the cost of twice the difference in heats of formation of propane (-25.0 kcal mol^{-1})[7] and isopropyl radical. A coetaneous value, 16.7 kcal mol^{-1},[9] for the latter pointed to an estimated enthalpy of formation for cyclohexa-1,4-diyl (54.0 kcal mol^{-1}) seductively close to the experimental enthalpy of formation of the transition region (53.6 kcal mol^{-1}) of the archetypal Cope rearrangement. This model attracted extensive attention, particularly in its theoretically more proper reformulation by Dewar et al. as a biradicaloid.[10] As the enthalpy of formation of isopropyl radical gradually rose with time, finally to reach the value 21.3 kcal mol^{-1},[11] the estimated enthalpy of formation of cyclohexa-1,4-diyl rose to 63.5 kcal mol^{-1}, some 10 kcal mol^{-1} above the experimental transition region.

Phenyl in the "Chameleonic" Domain. "State-of-the-art" theoretical calculations of the "aromatic" (concerted) transition structure of the archetype define its geometry and enthalpy.[12–14] All agree that the "potential energy surface ... is flat". Over the range from 1.64 Å ("diradicaloid" but far from "diradical") through a minimum at 1.85 Å (the "aromatic" transition

structure) to 2.19 Å, the spread in enthalpy is no more than ~3 kcal mol^{-1} (at 0° K).[14] The continuum, as originally formulated in detail by Dewar and Wade,[10] elaborated by Wehrli, Schmid, Belluŝ, and Hansen,[15] and Gajewski and Conrad,[16] is here designated "chameleonic". The core six-membered ring of the transition structure in its chairlike conformation is characterized by C_{2h} symmetry and equality of the critical bond distances, C-3–C-4 and C-1–C-6. Owing to its calculated flatness, this depiction of the transition region offers little prospect of serving usefully as a model for the perturbational approach. There are no rules either for deciding where to hang a particular perturbation along the continuum from 1.64 to 2.19 Å or beyond, or for estimating the magnitude of a hypothetical optimum thermochemical response. These remarks do not detract from the notable successes achieved in calculating de novo the enthalpies of activation of Cope rearrangements perturbed by nitrile and vinyl groups.[17,18]

A conceptual scheme compatible with the calculated flatness can be envisioned and evaluated quantitatively on the basis of a division of radical-stabilizing perturbations according to their location in hexa-1,5-diene. By analogy with their expected effect on an allyl radical, an "active" category located at C-1, C-3, C-4, or C-6 and an inactive, "nodal" category at C-2 or C-5 can be defined. Radical-stabilizing perturbations in active positions may be expected to shift the transition region toward the bis-allyl radical extreme, whereas in nodal positions they become active by shifting the transition region toward the cyclohexadiyl extreme. Testing the validity of this approach begins with an examination in the chameleonic domain of perturbations by the phenyl group in active and nodal locations. Only three patterns of substitution satisfy the specification: 2,5-diphenyl- (nodal), 1,4-diphenyl- (active),[19] and 1,3,4,6-tetraphenylhexa-1,5-diene (active) (see Figure 2).[20]

Dewar and Wade[21] selected 2,5-diphenyl-3,3,4,4-d_4-hexa-1,5-diene as a candidate to bring about a change in mechanism toward the cyclohexa-l,4-diyl biradicaloid. The rearrangement occurred so much faster than the archetype ($\Delta H^{\ddagger} = 21.3 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -20.8 \pm 0.5$ cal mol^{-1} K^{-1}; reproduced using the 1,6-^{13}C-labeled isotopomer)[22] that this supposition was considered verified. It remained to ask whether the full stabilizing capacity of phenyl had been realized.

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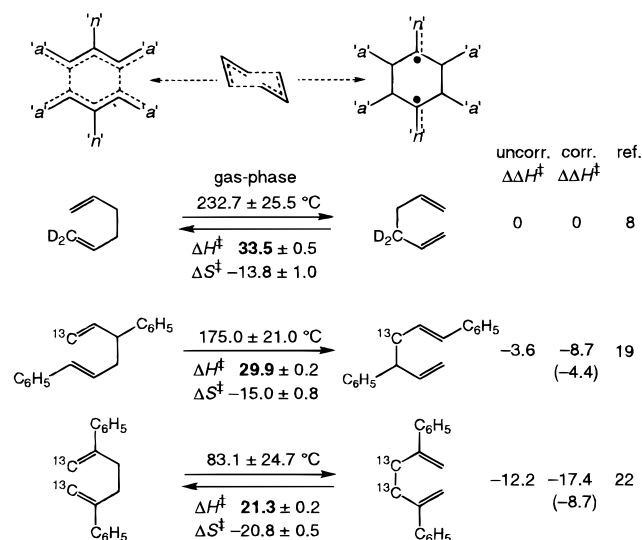
Figure 2. 1,4-Diphenyl- and 2,5-diphenyl-hexa-1,5-diene are perturbed symmetrically in active ("*a*") and nodal ("*n*") positions, respectively. Activation parameters are reported: $\Delta H^{\ddagger}$ in kcal mol^{-1} and $\Delta S^{\ddagger}$ in cal mol^{-1} K^{-1}. Discrepancies from the archetype (33.5 kcal mol^{-1}) are given uncorrected (uncorr. $\Delta \Delta H^{\ddagger}$), and corrected (corr. $\Delta \Delta H^{\ddagger}$) for the lowering in enthalpy of formation of the educt by conjugative interaction.

The answer requires *quantitative* examination of the enthalpy of activation. Analysis begins obligatorily with correction for conjugation in the educt. Reliable values for conjugative interactions of phenyl (and alkyl) *vis-à-vis* hydron, *inter alia* in four distinct types of environment, are reproduced in Figure S1 of Supporting Information.[23,24] With phenyl, values range from -5.1 kcal mol^{-1} for β-alkyl substituted to -2.6 kcal mol^{-1} for α-alkyl substituted styrenes, the type involved in this example.[25,26] Were conjugation the only effect of perturbations in the 2 and 5 positions, the predicted enthalpy of activation would be raised to 38.7 ($33.5 + 2 \times 2.6$) kcal mol^{-1} ($\Delta \Delta H^{\ddagger}_{o} + \Delta H_{ci}$ in Figure 1). The experimental value, 21.3 kcal mol^{-1}, is lower by -17.4 kcal mol^{-1} or -8.7 kcal mol^{-1} per phenyl group. As large as this stabilization may seem, does it reflect the full stabilization that a phenyl group is able to provide a simple radical?

Although there is an extensive literature on the stabilization energy in a benzyl radical, there is no *direct* evaluation of the bond dissociation enthalpy (BDE) of the tertiary benzylic CH bond. An indirect estimate is available from Denisov's collection and analysis of the rates of all the radical abstractions from hydrocarbons in the literature.[27] In particular, he has deduced a BDE for phenylcyclohexane of 83.6 kcal mol^{-1} relative to that of toluene as standard, taken to be $\Delta H_{298} = 88.0$ kcal mol^{-1}. This value being 1.8 kcal mol^{-1} lower than the value for toluene,

89.8 ± 0.6 kcal mol^{-1}, most recently favored by Ellison *inter alios*,[28] Denisov's value is corrected to 85.4 kcal mol^{-1}. Subtraction of the standard enthalpy of formation of hydron, 52.1 kcal mol^{-1}, leads to $\Delta \Delta_f H^o = +33.3$ kcal mol^{-1} as the *change* in enthalpy of formation in the transformation of phenylcyclohexane to phenylcyclohexyl radical (and one half dihydrogen). The difference between this value and $+44.3$ kcal mol^{-1}, $\Delta \Delta_f H^o$ for the transformation of isobutane into the *tert*-butyl radical,[7] is -11.0 kcal mol^{-1}. Greater than the value of -8.7 kcal mol^{-1} per phenyl group deduced above, it points to substantial, but not full, realization of the stabilizing potential.

The validity of having selected the "aromatic" archetype as model (33.5 kcal mol^{-1}) is arguable. If the two phenyl groups have indeed shifted the transition region close to the diradical extreme of the chameleonic continuum, a more apppropriate model is *unstabilized* 1,4-diphenylcyclohexa-1,4-diyl.[29] From an enthalpy of formation of 2,5-diphenylhexa-1,5-diene,[30] addition of the experimental enthalpy of activation (21.3 kcal mol^{-1}) leads to an "experimental" enthalpy of formation of the transition region of $+87.9$ kcal mol^{-1}. This value is lower by -22.2 kcal mol^{-1} or -11.1 kcal mol^{-1} per phenyl group than the enthalpy of formation of 110.1 kcal mol^{-1} estimated for the unstabilized diradical.[29] The phenyl groups have stabilized the transition region quantitatively *as if* it were simulating cyclohexa-1,4-diyl (overview in Supporting Information, Figure S5).

To the extent that a chair model of 1,4-diphenylcyclohexa-1,4-diyl is consistent with experiment, conformations in the bicyclo[2.2.0]hexane domain of the Cope potential energy surface are also viable (see Scheme 1).[31] Although Goldstein and Benzon in their elegant investigation of the archetype rejected the intervention of twist-boat-cyclohexa-l,4-diyl[32] in stereochemical inversion and cleavage to hexa-1,5-diene on the basis of the erroneously low enthalpy of formation of the isopropyl radical, it is now a serious contender, the more so in light of recent theoretical results of Baumann and Voellniger-Borel.[33] The proposition is developed at greater length in Supporting Information, Appendix S1, Figures S3, S4, and S5.

Although the phenyl group may still be too large for successful calculations at the level required to handle hexa-1,5-diene, Beno et al. have made theoretical calculations on the

(23) In the publication,[24] heats of formation of a few of the relevant phenyl hydrocarbons were based redundantly on a mean of values that included those few experimental values noted and those calculated by the method of group equivalents, which, of course, had been based on the same data but gave somewhat different results. Recalculations that omit the latter values have led to a few quite minor modifications.

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(25) Note the discrepancy, for which we offer no explanation, of 0.6 kcal mol^{-1} between the heats of hydrogenation of styrene *predicted* from the equilibrium data (-27.52) (Figure S1 of Supporting Information) and *determined* by combustion (-28.20)[7] and hydrogenation (-28.01).[26]

(26) Abboud, J.-L.; Jiménez, P.; Roux, M. V.; Turrión, C.; Lopez-Mardomingo, C.; Podosenin, A.; Rogers, D. W.; Liebman, J. F. *J. Phys. Org. Chem.* **1995**, *8*, 15−25.

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(28) Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrosc.* **1996**, *156*, 109−131.

(29) An estimated $\Delta_f H^o = +21.5$ kcal mol^{-1} for 1,4-diphenylcyclohexane is derived from cyclohexane (-29.49 kcal mol^{-1}) and phenylcyclohexane (-3.99 kcal mol^{-1}): $\Delta \Delta_f H^o = +25.50$ kcal mol^{-1}.[7] Removal of two hydrons using the currently "best" value for the tertiary CH bond in isobutane ($\Delta \Delta_f H^o = +44.3$ kcal mol^{-1}) leads to an enthalpy of formation of $+110.1$ kcal mol^{-1} (Supporting Information, Figure S5).
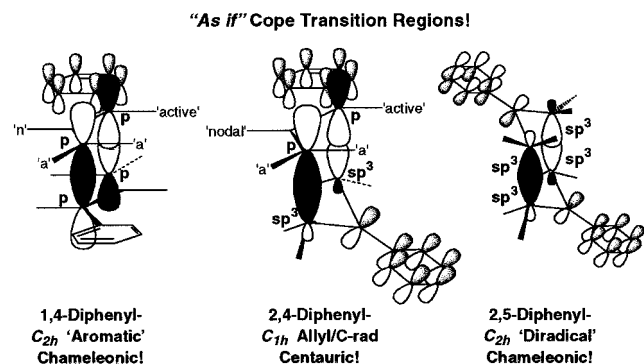
(30) Although the heat of formation of 2,5-diphenylhexa-1,5-diene is reported to be $+68.0$ kcal mol^{-1} on the basis of its heat of hydrogenation (ΔH_{H2} 56.65 kcal mol^{-1}), reservations stem from finding $\Delta H_{H2} = 55.65$ kcal mol^{-1} for its homolog, 2,6diphenylhepta-1,6-diene.[22] An altenative value is derived from 2,5-diphenylhexane: calculated $\Delta_f H^o = +11.88$ kcal mol^{-1} [*n*-hexane, -39.94 kcal mol^{-1}]; $\Delta \Delta_f H^o = +25.91$ kcal mol^{-1} (isopropylbenzene, $+0.96$ kcal mol^{-1}/propane, -25.02 kcal mol^{-1}; 2-phenylbutane, -4.16 kcal mol^{-1}/*n*-butane; -30.00 kcal mol^{-1}).[7] Addition of twice the appropriate heat of dehydrogenation, 27.34 kcal mol^{-1}, estimated from van't Hoff studies, generates $\Delta_f H^o$ for 2,5-diphenylhexa-1,5-diene of $+66.6$ kcal mol^{-1}. By the same method, $\Delta_f H^o = +7.0$ kcal mol^{-1} is calculated for 2,6-diphenylheptane and $+61.7$ kcal mol^{-1} for 2,6-diphenylhepta-1,6-diene.

(31) Roth, W. R.; Klärner, F.-G.; Lennartz, H.-W. *Chem. Ber.* **1980**, *113*, 1818−1829.

(32) (a) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 5119−5121; (b) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7147−7149; (c) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7149−7151; (d) Benzon, M. S., Ph.D. Dissertation, *Diss. Abstr. Intern. B* 1972, Vol. 45, p 1468B (Order-No. 72-18547).

(33) Baumann, H.; Voellinger-Borel, A. *Helv. Chim. Acta* **1997**, *80*, 2112−2122.

Scheme 2

"As if" Cope Transition Regions!

1,4-Diphenyl-
C_{2h} 'Aromatic'
Chameleonic!

2,4-Diphenyl-
C_{1h} Allyl/C-rad
Centauric!

2,5-Diphenyl-
C_{2h} 'Diradical'
Chameleonic!

rearrangement of apposite vinylhexa-1,5-dienes. Conventionally estimated thermochemical properties are outlined in Figure S6 of Supporting Information. On the entirely reasonable assumption that the vinyl group is a good simulacrum of the phenyl group,[18] the theoretically predicted enthalpy of activation of -20.9 kcal mol^{-1} agrees well with the experimental value for 2,5-diphenylhexa-1,5-diene, 21.3 kcal mol^{-1}. A value of 24.4 kcal mol^{-1}, reported by Roth et al.[34] for the rearrangement of 3-ethylidene-5-methyl-6-methylene-octa-1,7-diene, after correction for the single element of methyl conjugative interaction in the educt (2.7 kcal mol^{-1}), is also in excellent agreement with that predicted by Beno et al.[18]

Substitution in active positions in the chameleonic domain is exemplified by l,4-diphenylhexa-1,5-diene ($\Delta H^{\ddagger} = 29.9 + 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -15.0 \pm 0.8$ cal mol^{-1} K^{-1}).[19] After the single correction for conjugative interaction of 5.1 kcal mol^{-1}, the enthalpy of activation is lower than that of the archetype ($29.9 - 33.5 - 5.1 = -8.7$ kcal mol^{-1}) by -4.4 kcal mol^{-1} per phenyl group (Figure 2). This stabilization corresponds satisfactorily to three values reported for cinnamyl radical relative to allyl radical: -3.6,[35] -5.3,[36,37] and -5.4 kcal mol^{-1}.[38] Perturbation in active positions like those in nodal positions appear to have behaved *"as if"* full stabilization had been realized.

Another, perhaps flawed, example is that of *rac*-3,4-diphenylhexa-1,5-diene, which is afflicted with a large thermochemical bias of -10.2 kcal mol^{-1} in favor of the product. Studied by Koch,[39] Lutz and Berg,[40] and Klärner et al.,[41] the lowering in enthalpy of activation corresponds to -4.7 per phenyl group ($\Delta H^{\ddagger} = 24.0 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -12.4 \pm 0.6$ cal mol^{-1} K^{-1}) in excellent agreement with the lowering seen in 1,4-diphenylhexa-1,5-diene.

Phenyl in the Centauric Domain. In the centauric domain, two sets of substituents are brought into conflict: one set in "active" positions draws toward the allylic transition region, while a second in the "nodal" position draws toward the cyclohexadiyl region (Scheme 2).[42] Is the transition region obliged to retain chameleonic symmetry with the possible

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(35) Doering, W. v. E.; Benkhoff, J.; Shao, L.-m. *J. Am. Chem. Soc.* **1999**, *121*, 962−968.

(36) R. Wiktor in footnote 129, Scheme 17 and Table 39 of ref 37. See also ref 34.

(37) Roth, W. R.; Staemmler, V.; Neumann, M.; Schmuck, C. *Liebigs Ann.* **1995**, 1061−1118. See especially pp 1095, 1100, 1101; Table 48, p 1104.

(38) Saltiel, J.; Crowder, J. M.; Wang, S. *J. Am. Chem. Soc.* **1999**, *121*, 895−902.

(39) Koch, H. P. *J. Chem. Soc.* **1948**, 1111−1117.

(40) Lutz, R. P.; Berg, H. A. *J. Org. Chem.* **1980**, *45*, 3915−3916.

(41) Diedrich, M. K.; Hochstrate, D.; Klärner, F.-G.; Zimny, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1079−1081.

		gas-phase		uncorr. $\Delta\Delta H^{\ddagger}$	corr. $\Delta\Delta H^{\ddagger}$	ref.
		232.7 ± 25.5 °C		0	0	8
		$\Delta H^{\ddagger}$ **33.5** ± 0.5				
		$\Delta S^{\ddagger}$ −13.8 ± 1.0		$\Delta\Delta H^{\ddagger} = -4.2$		
		160.0 ±10.0 °C		−4.2	−6.8	21
		$\Delta H^{\ddagger}$ **29.3** ± 1.6				
		$\Delta S^{\ddagger}$ −9.9 ± 3.6				
		182.7 ± 17.3 °C		−5.4	−5.4	21
		$\Delta H^{\ddagger}$ **28.1** ± 0.4				
		$\Delta S^{\ddagger}$ −16.8 ± 1.0		$\Delta\Delta H^{\ddagger} = -3.5$		
		140.0 ± 20.0 °C		−8.9	−11.5	21
		$\Delta H^{\ddagger}$ **24.6** ± 0.8				
		$\Delta S^{\ddagger}$ −16.9 ± 0.7				
		175.0 ± 21.0 °C		−3.0	−8.1	this work
		$\Delta H^{\ddagger}$ **30.5** ± 0.3				
		$\Delta S^{\ddagger}$ −14.6 ± 0.7		$\Delta\Delta H^{\ddagger} = -2.8$		
		143.0 ± 21.8 °C		−5.8	−13.5	this work
		$\Delta H^{\ddagger}$ **27.7** ± 0.1				
		$\Delta S^{\ddagger}$ −15.4 ± 0.3				
		B/H calc.		−3.1	−8.6	18
		$\Delta H^{\ddagger}$ **30.4**				
		B/H calc.		−3.6	−10.1 (−5.1)	18
		$\Delta H^{\ddagger}$ **29.9**				
		B/H calc.		−3.1	−15.1	18
		$\Delta H^{\ddagger}$ **30.4**				

Figure 3. Three examples in the centauric domain involve the pairs in rows 1 and 2, 3, and 4, and 5 and 6. The lowering in enthalpy of activation on replacing an allyl moiety by a 2-phenylallyl moiety is interpolated as $\Delta\Delta H^{\ddagger}$. Deviations from the archetype (-33.5 kcal mol^{-1}) are given uncorrected (uncorr. $\Delta\Delta H^{\ddagger}$) and corrected (corr. $\Delta\Delta H^{\ddagger}$) for conjugative interaction in the educt. In the lower part, the results of theoretical calculations on vinyl analogs by Beno et al. are recorded. $\Delta H^{\ddagger}$ values are in kcal mol^{-1}; $\Delta S^{\ddagger}$ values are in kcal mol^{-1} K^{-1}.

consequence that the stronger of the perturbations *alone* will prevail? Or will the symmetry change to "centauric" so that one half functions *as if* it were an allylic radical, while the other functions *as if* it were a tertiary aliphatic radical? Perhaps a compromise is reached that denies each competing perturbation from realizing its full stabilizing potential. Resolution comes in the form of *quantitative* distinctions.

In the literature, the example of 2,4-diphenylhexa-1,5-diene was designed by Dewar and Wade to test the hypothesis of additivity. Based on full use of the stabilization energies of -4.4 kcal mol^{-1} per "*a*" phenyl and -8.7 kcal mol^{-1} per "*n*" phenyl (Figure 2), restriction to the chameleonic domain leads to a predicted enthalpy of activation of 27.4 kcal mol^{-1} ($33.5 + 2.6 - 8.7$ kcal mol^{-1}). In the centauric domain, a minimum enthalpy of activation of 23.0 kcal mo1^{-1} ($33.5 + 2.6 - 4.4 - 8.7$ kcal mol^{-1}) is predicted. Based on the values from 2- and 3-phenylhexa-1,5-dienes in Figure 3, another predicted value is 23.9 kcal mol^{-1} ($33.5 + 2.6 - 5.4 - 6.8$ kcal mol^{-1}). Both are in satisfactory agreement with experiment ($\Delta H^{\ddagger} = 24.6 + 0.8$ kcal mol^{-1}) and support the centauric model, but not the chameleonic

(42) Centauric, half man, half horse, is intended as a mnemonically keen sobriquet. A referee suggests a happy alternative: minotauric.

Table 1. Specific Rate Constants and Derived Activation Parameters for the Reversible Rearrangement of 1,3-Diphenylhexa-1,5-diene-6-^{13}C in Benzene-d_6

T, °C	$k_1 \times 10^6$ s^{-1} [a]
154.0 ± 0.3	1.51 ± 0.01
165.0 ± 0.5	3.72 ± 0.04
176.8 ± 0.2	9.60 ± 0.09
185.2 ± 0.1	19.07 ± 0.11
196.0 ± 0.1	40.37 ± 0.34
Arrhenius parameters	$E_a = 31.36 \pm 0.28$ kcal mol^{-1}
	$\log A = 10.22 \pm 0.14$
Eyring parameters[b]	$\Delta H^{\ddagger} = 30.5 \pm 0.3$ kcal mol^{-1}
	$\Delta S^{\ddagger} = -14.6 \pm 0.6$ kcal mol^{-1} K^{-1}

[a] Calculated by linear regression of the standard expression for reversible first-order reactions. [b] Calculated at 175 °C.

Table 2. Specific Rate Constants and Derived Activation Parameters for the Reversible Rearrangement of 1,3,5-Triphenylhexa-1,5-diene-6-^{13}C in Benzene-d_6

T, °C	$k_1 \times 10^6$ s^{-1} [a]
121.2 ± 0.1	1.73 ± 0.01
132.0 ± 0.1	4.65 ± 0.06
144.6 ± 0.1	13.33 ± 0.10
152.1 ± 0.1	24.61 ± 0.11
164.8 ± 0.1	64.81 ± 0.31
Arrhenius parameters	$E_a = 28.49 \pm 0.09$ kcal mol^{-1}
	$\log A = 10.03 \pm 0.09$
Eyring parameters[b]	$\Delta H^{\ddagger} = 27.7 \pm 0.09$ kcal mol^{-1}
	$\Delta S^{\ddagger} = -15.4 \pm 0.3$ kcal mol^{-1} K^{-1}

[a] Calculated by linear regression of the standard expression for reversible first-order reactions. [b] Calculated at 143 °C.

model. Although the superiority of the centauric model seems clear, there is a small shortfall from full centauric expectation that may be real or little more than a reflection of experimental uncertainties. If real, it is important for theory and for the use of the model for predictive purposes.

In a new test of the centauric model presented here, 1,3-diphenylhexa-1,5-diene and 1,3,5- triphenylhexa-1,5-diene are compared. Both are degenerate and therefore uncompromised by thermochemical bias. For kinetic examination, 1,3-diphenylhexa-1,5-diene is labeled at C-6 with ^{13}C. The resulting specific rate constants and derived activation parameters are given in Table 1 (175.0 + 21.0 °C). The enthalpy of activation, $\Delta H^{\ddagger} = 30.5 \pm 0.3$ kcal mol^{-1} ($\Delta S^{\ddagger} = -14.6 \pm 0.9$ cal mol^{-1} K^{-1}),[43] after correction by -5.1 kcal mol^{-1} for conjugative interaction in the educt, reveals a lowering of -8.1 kcal mol^{-1} by the 1,3-diphenylallyl group (rows 1 and 5 of Figure 3). This lowering compares with that of -5.4 kcal mol^{-1} by the 3-phenylallyl group (row 3).

Because 1,3-diphenylhexa-1,5-diene is centauric and not a model chameleon, 1,3,4,6-tetraphenylhexa-1,5-diene might be considered a better model, but appears to present special problems as a consequence of its closeness to the homolytic-colligative regime. Racemization of the optically active (*E,E*) isomer has activation parameters, $\Delta H^{\ddagger} = 21.3 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -13.2 \pm 0.3$ cal mol^{-1} K^{-1}.[20] After correction by -10.2 kcal mol^{-1} for conjugative interaction in the educt, an empirical lowering of -22.4 kcal mol^{-1} by the two 1,3-diphenylallyl groups emerges. That the additional lowering by the second 1,3 diphenyl group should have been so large as -14.3 kcal mol^{-1} finds no conventional explanation in our hands. Beno et al. have, however, uncovered a significant cooperative augmentation in their comparison of 1,3-dicyano-and l,3,4,6-tetracyano-hexa-1,5-diene. In their credible rationalization, the first set of perturbations moves the transition region in the allylic direction and thereby allows the second concordant set to be more effective than the first alone.

1,3,5-Triphenylhexa-l,5-diene incorporates the competing effects of the doubly "active" 1,3-diphenyl group and the "nodal" 5-phenyl group. Specific rate constants are determined in benzene solution on a sample labeled with ^{13}C at C-6 over the temperature range, 143.0 ± 21.8 °C (Table 2). The system, which is perturbed by two elements of conjugative interaction (33.5 + 5.1 + 2.6 kcal mol^{-1}), is predicted to have an enthalpy of activation of 41.2 kcal mol^{-1}, absent stabilization in the transition region. The experimental enthalpy of activation, $\Delta H^{\ddagger} =$

27.7 ± 0.1 kcal mol^{-1} ($\Delta S^{\ddagger} = -15.4 \pm 0.3$ cal mol^{-1} K^{-1}), is lower by -13.5 kcal mol^{-1}. This stabilization is substantially greater than that expected of either the 1,3-diphenyl moiety (-8.1 kcal mol^{-1}) or the 5-phenyl moiety (-6.8 kcal mol^{-1}) working alone in a C_{2h} chameleonic domain (Figure 2). Here, too, there is a possibly significant shortfall from the full centauric expectation of their sum, -14.9 kcal mol^{-1}, based on the two stabilizing groups working optimally and independently.[44]

Recent theoretical calculations by Beno et al. on vinyl-, 1,3-divinyl-, and 1,3,5-trivinyl-hexa-1,5-diene as reasonable surrogates for the trio of phenylhexadienes predict enthalpies of activation of 30.4, 29.9, and 30.4 kcal mol^{-1}, respectively. Direct comparison with the archetype (33.5 kcal mol^{-1}) (uncorr. $\Delta\Delta H^{\ddagger}$) reveals that 1,3,5-trivinylhexa-1,5-diene is slightly destabilized relative to the chameleonic model, -3.1 kcal mol^{-1} versus either -3.1 kcal mol^{-1} (2-vinyl-) or -3.6 kcal mol^{-1} (1,3-divinyl), and strongly destabilized vis-à-vis the value predicted on the basis of the centauric model (-6.7 kcal mol^{-1}). A quite different picture in gratifying agreement with the thesis of this work emerges if credit is given for the enthalpy consumed in overcoming the estimated conjugative interaction in the educts.[45] The requisite enthalpies of conjugation of vinyl vis-à-vis hydron are estimated to be -6.5 kcal mol^{-1} for *trans*-piperylene and -5.5 kcal mol^{-1} for isoprene, models for 1,3-divinyl- and 2-vinyl-hexa-1,5-diene, respectively (for details, see Figure S2 of Supporting Information). The corrected value of $\Delta\Delta H^{\ddagger}$ given in the lower part of Figure 3 (-15.1 kcal mol^{-1} predicted) is now closer to the centauric model (-18.7 kcal mol^{-1}; chameleonic, -10.1 kcal mol^{-1}). Comparison of experimental corr. $\Delta\Delta H^{\ddagger}$ for phenyl perturbations and theoretical for corresponding vinyl compounds in Figure 3 is remarkably favorable, with the exception of the experimentally questionable 2-phenylhexadiene.

Conclusions

A conceptual scheme for handling perturbations on Cope's rearrangement of hexa-1,5-diene recognizes two types: one located at positions 1, 3, 4, or 6, the "active" positions, and a second at 2 or 5, the "nodal" positions. Radical-stabilizing substituents in the first locus seem to behave *as if* they draw

(43) Emrani, J., Ph.D. Dissertation, Indiana University, 1985 (Gajewski, J. J., Research Sponsor); *Diss. Abstr. Intern.* 1985, Vol. 46, p 1922B (Order No.: 85 16636) ($\Delta H^{\ddagger} = 29.0 \pm 1.4$ kcal mol^{-1}; $\Delta S^{\ddagger} = -16.3 \pm 3.1$ cal mol^{-1} K^{-1}, our calculation from his data).

(44) Note that the values from the purely chameleonic models could be used, whereupon the expected lowering from the 1,3-diphenyl portion, -11.2 kcal mol^{-1}, and the 5-phenyl portion, -8.7 kcal mol^{-1}, together would have amounted to -19.9 kcal mol^{-1}. Not only have we stated reservations about the appropriateness of 1,3,4,6-tetraphenylhexa-1,5-diene as model, but the cooperational augmentation indicated by theoretical calculations also argues against its use.

(45) Note that replacement of allyl by 2-vinylallyl in 1,3-divinylhexa-1,5-diene is destabilizing by $+0.5$ kcal mol^{-1} if uncorrected enthalpies of activation are considered.

the transition region toward the extreme of a pair of allyl radicals, even though that end of the continuum is the more difficultly achievable for two reasons: first, because a total stabilization of 26 kcal mol^{-1} is needed (quite apart from enthalpy to counter whatever deceleration might have been occasioned by conjugative interaction in the educt); and, second, because perturbation in the active locus of an allyl radical is considerably less effective than is perturbation of a tertiary radical. That a perturbation of the first type should be comparable in magnitude to its effect on a simple allyl radical seems all the more remarkable. By contrast, perturbations in the second locus have to overcome only 10 kcal mol^{-1} in order to approach the other, cyclohexa-1,5-diyl diradical end of the continuum. In this type also, the major part of the potential stabilization of a tertiary alkyl radical seems to be realized. Multiple perturbations are divided into two classes. One is defined as the "chameleonic", in which every perturbation occupies the same type of locus, and the core of the chair-like six-membered ring of the transition region retains C_{2h}-like symmetry. The other is defined as the "centauric" of C_{1h} symmetry, in which one half of the transition region is perturbed at "active" positions, the other at a "nodal" position. In the chameleonic domain, the two identical halves are pulled toward either the bis-allylic or the cyclohexa-1,5-diyl extreme; in the centauric domain, the two halves are free to be drawn in opposing directions (Figure 3). The question, "How are the conflicting demands resolved?", is answered in favor of the centauric. Each perturbation seems to contribute its full stabilizing potential independently, or close to it.

Reviewed oversimplistically, replacement of an allyl moiety in hexa-1,5-diene, 3-phenyl-, and 3,5-diphenyl-hexa-l,5-diene by competing moiety 2-phenylallyl, lowers the enthalpy of activation vis-à-vis the archetype by $\Delta\Delta H^{\ddagger} = -4.2, -3.5,$ and -2.8 kcal mol^{-1}, respectively. Were this sequence a trend toward less effective competition by the nodal half as the active half becomes stronger—one should caution that ± 1 kcal mol^{-1} may already be a generous assessment of accuracies—substantiation by further experiment and theory would be required prior to its incorporation into the conceptual scheme for handling perturbations.

Experimental Section

General Procedures. ^{1}H NMR and ^{13}C NMR (125.8 MHz) spectra were measured in benzene-d_6 on a Bruker AM-500 instrument (500 MHz unless otherwise noted). Spin-lattice relaxation times (T_1) were determined by the inversion-recovery method with use of vacuum-sealed solutions in benzene-d_6. Chemical shifts are reported in parts per million (δ); coupling constants, *J,* are reported in hertz. High-resolution mass spectra (HRMS) were measured on a JEOL AX 505 spectrometer equipped with a data-recovery system and reported as *m/z* (density as percent of major peak). Melting points are uncorrected. Solvents were redistilled before use: THF from sodium/benzophenone, benzene from P$_2$O$_5$. A *standard work-up* consisted of quenching with saturated aqueous NH$_4$Cl, extraction first with diethyl ether, then with CH$_2$Cl$_2$, drying the combined organic layers over anhydrous MgSO$_4$, filtration, concentration to an oil, and flash column chromatography (hexane as eluting solvent).

(*E*)-1,3,5-Triphenyl-1,5-hexadiene. The starting material, (*E,E*)-cinnamylideneacetophenone, was prepared from *trans*-cinnamaldehyde and acetophenone following Scholtz:[46] ^{1}H NMR (300 MHz) 6.43 (d, *J* = 15.6, 1H), 6.63 (dd, *J* = 15.7, *J* = 11.0, 1H), 6.78 (d, *J* = 14.9, 1H), 7.05 (m, 8H), 7.64 (dd, *J* = 14.9, *J* = 11.0, 1H), 7.92 (d, *J* = 10.3, 2H). It was converted to (*E*)-1,3,5-triphenyl-4-pentenone following

the procedure of Wibaut et al.:[47] ^{1}H NMR (300 MHz) 3.12 (d, *J* = 7.0, 2H), 4.38 (m, 1H), 6.36 (m, 2H), 7.09 (m, 13 H), 7.76 (d, *J* =7.0, 2H). A sample (0.53 g, 1.70 mmol) in 5 mL of THF was added dropwise with stirring to a solution of methyltriphenylphosphonium ylid, prepared from 0.88 g (2.48 mmol) of methyltriphenylphosphonium bromide and 0.99 mL of BuLi (2.5 M in hexane) in 20 mL of THF at 0 °C. After having been stirred at 0 °C for 1.5 h, the reaction mixture was diluted with 15 mL of THF and subjected to the *standard work-up*: 0.3 g (57%) as a colorless viscous oil; ^{1}H NMR 2.90 (d, *J* = 7.6, 2H), 3.55 (dt, *J* = 7.2, *J* = 7.6, 1H), 5.04 (d, *J* = 13.6, 2H), 6.21 (d; *J* = 15.9, 1H), 6.27 (dd, *J* = 7.2, *J* = 15.9, 1H), 7.01−7.16 (m, 13H), 7.26 (d, *J* = 7.1, 2H); MS *m/e* 311 (M + 1, 5.6); 310 (M, 15.9), 251 (M − 59, 17.6), 219 (M − 91, 6.8), 193 (M − 117, 100), 178 (13.5), 115 (30); HRMS calcd for (M$^+$) 310.1722, found 310.1724.

(*E*)-1,3,5-Triphenyl-1,5-hexadiene-6-^{13}C was prepared similarly using methyl-^{13}C-triphenylphosphonium iodide: ^{1}H NMR 2.90 (d, *J* = 7.6, *J* = 5.8, 2H), 3.55 (dt, *J* = 7.2, *J* = 7.6, 1H), 5.04 (d, *J* = 133.7, *J* = 155.9, 2H), 6.21 (d, *J* = 15.9, 1H), 6.27 (dd, *J* = 7.2, *J* = 15.9, 1H), 7.01−7.16 (m, ^{13}H), 7.26 (d, *J* = 7.1, 2H); MS *m/e* 311 (M, 9.8), 220 (M − 91, 6.4), 193 (M − 117, 100), 178 (18), 115 (36), 91 (7.4); HRMS calcd for (M$^+$) 311.1756, found 311.1742.

(E)-3,5-Diphenyl-4-pentenal. To a stirred solution of LDA, prepared from 7 mL (50 mmol) of diisopropylamine and 20 mL (50 mmol) of BuLi (2.5 M in hexane) in 40 mL of THF at −78 °C, was added a solution of 9.7 g (50 mmol) of (*E*)-l,3-diphenylpropene[48] in 50 mL of THF, dropwise. The resulting red solution was added dropwise with stirring at 78 °C for 2 h to a solution of 5.2 mL (50 mmol) of 2-bromomethyl-1,3-dioxotane at room temperature. The rate of addition was controlled by observing the disappearance of the red color. After completion of the addition, the reaction mixture was stirred for 1 h. *Standard work-up* without flash chromatography afforded an oil, which had an NMR spectrum consistent with the expected intermediate acetal. Without further purification, this material was treated with 5% H$_2$SO$_4$ in refluxing dioxane for 1 h. *Standard work-up* (10:1 hexane/EtOAc as the eluting solvent) afforded 9.44 g (80 %) of (*E*)-3,5-diphenyl-4-pentenal: ^{1}H NMR 2.36 (d, *J* = 7.4, 2H), 3.81 (dt, *J* = 7.4, *J* = 7.1, 1H), 6.13 (dd, *J* = 15.9, *J* = 7.1, 1H), 6.26 (d, *J* = 15.9, 1H), 7.03−7.18 (m, 10H), 9.31 (s, 1H); MS 237 (M + 1, 12), 236 (M, 59), 208 (M − 28, 38), 193 (M − 43, 78), 178 (M − 58, 34), 115 (100), 91 (34); HRMS calcd for (M$^+$) 236.1201, found 236.1195.

(E)-1,3-Diphenyl-1,5-hexadiene. A solution of the aldehyde above (0.54 g, 2.3 mmol) in 5 mL of THF was added dropwise with stirring to a solution of methyl triphenylphosphonium ylid, prepared from 0.89 g (2.5 mmol) of methyltriphenylphosphonium bromide and 10 mL of BuLi (2.5 M in hexane) in 20 mL of THF at 0 °C. After 1 h at 0 °C, *standard work-up* gave 0.3 g (57%) of (*E*)-1,3-diphenyl-1,5-hexadiene as a colorless oil: ^{1}H NMR 2.48 (dd, *J* = 6.9, *J* = 7.3, 2H), 3.39 *(*dt, *J* = 15.9, *J* = 7.3, 1H), 5.00 (dd, *J* = 21.1, *J* = 17.2, 2H), 5.74 (m, 1H), 6.29 (dd, *J* = 15.9, *J* = 6.9, 1H), 6.35 (d, *J* = 15.9, 1H), 7.04−7.23 (m, 10H); MS 234 (M, 1.7), 193 (M − 41, 100), 178 (M − 56, 27), 165 (M − 69, 15), 115 (M − 119, 70), 91 (29), 78 (59); HRMS calcd for (M$^+$) 234.1409, found, 234.1416.

In similar fashion, (*E*)-1,3-diphenylhexa-1,5-diene-6-^{13}C was prepared using methyl-^{13}C-triphenylphosphonium iodide: ^{1}H NMR 2.48 (ddd, *J* = 6.9, *J* = 7.3, *J* = 5.8, 2H), 3.39 (dt, *J* = 15.9, *J* = 7.3, 1H), 5.00 (ddd, *J* = 155.1, *J* = 22.7, *J* = 17.1, 2H-), 5.74 (m, 1H), 6.29 (dd, *J* = 15.9, *J* = 6.9, 1H), 6.35 (d, *J* = 15.9, 1H), 7.04−7.23 (m, 10H); MS 235 (M, 3.8), 194 (M − 41, 58), 193 (M − 42, 100), 178 (M − 57, 37), 165 (14), 115 (86), 91 (20); HRMS calcd for (M$^+$) 235.1443, found 235.1441.

Kinetic Measurements. Kinetic studies were effected in degassed C$_6$D$_6$ (0.6 mL) in vacuum-sealed NMR tubes with CHDCl$_2$ as internal standard. The concentration of the diene used in the thermal rearrangements ranged from 0.034 M to 0.055 M. Heating was effected in the vapors of appropriate liquids boiling under reflux. The chosen liquids were distilled before use: undecane (196 °C), diethyl oxalate (185 °C), 4-methylanisole (176 °C), mesitylene (164 °C), anisole (154 °C), cumene (152 °C), *o*-xylene (144 °C), chlorobenzene (132 °C), and

(46) Scholtz, M. *Chem. Ber.* **1895**, *28*, 1726−1733.

(47) Wibaut, J.; Overhoff, J.; Jonker, E. *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 31−45.

(48) Raunio, E.; Bonner, W. *J. Org. Chem.* **1966**, *31*, 396−399.

tetrachloroethane (121 °C). The tubes were periodically withdrawn from the bath for analysis by ^{1}H-NMR and returned for further heating. Temperature was monitored by a thermocouple and read periodically during heating. An average value was taken for each analysis of data. For the kinetic measurements at higher temperatures, correction was made for the time taken for the reintroduced tube to reach the reaction temperature. This lag time (~40 s) was determined beforehand by introducing similar tubes containing a thermocouple.

Quantitative analysis by ^{1}H NMR took advantage of ^{13}C coupling with vinyl hydrons at C-6 and methylene hydrons at C-4 in both starting material and product. Recovery was monitored by comparing the benzylic hydron at C-3 (3.4 ppm) with the singlet at 4.2 ppm in the standard (CH$_2$Cl$_2$). Each datum was generated from at least three integrations while the final percentage of starting material and product was the average of the two sets of signals. Relaxation times were determined for each group of hydrons. The protocol involved an acquisition time of 2.77 s, relaxation delay times of 12 s for 1,3,5-triphenylhexa-1,5-diene-6-^{13}C and 19 s for 1,3-diphenylhexa-1,5-diene-6-^{13}C, and 32 scans for each measurement. Specific rate constants and activation parameters are given in Tables 1 and 2, based on data in Tables S1 and S2, respectively. Products of thermal rearrangement were identified by ^{1}H NMR: 1,3,5-triphenylhexa-1,5-diene-4-^{13}C 2.90 (dd, $J = 7.6$, $J = 128.4$, 2H), 3.55 (m, 1H), 5.04 (dd, $J = 133.7$, $J = 10.6$, 2H), 6.21 (d, 15.9, 1H), 6.27 (dd, $J = 15.9$, $J = 7.2$, 1H), 7.01−7.16 (m, 13H), 7.26 (d, 2H). 1,3-Diphenylhexa-1,5-diene-4-^{13}C: 2.48 (ddd, $J = 127.7$, $J = 6.9$, $J = 7.3$, 2H), 3.39 (m, 1H), 5.00 (m, 1H), 5.74 (m, 1H), 6.29 (dd, $J = 15.9$, $J = 6.9$, 1H), 6.35 (d, $J = 15.9$, 1H), 7.04−7.23 (m, 10H).

Supporting Information Available: Six figures, an appendix, and two tables give a collection of heats of hydrogenation of styrenes and alkenes, a derivation of the thermochemistry of 1- and 2-vinylhexa-l,5-dienes, a consideration of the possible role of bicyclo[2.2.0]hexane in the rearrangement of 2,5-diphenylhexa-l,5-diene, and kinetic data for Tables 1 and 2. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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