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Perturbation of the Degenerate, Concerted Cope Rearrangement by Two Phenyl Groups in "Active" Positions of (*E*)-1,4-Diphenylhexa-1,5-diene. Acceleration by High Pressure as Criterion of Cyclic Transition States

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Abstract: Previous examinations of radical-stabilizing substituents in the two distinct types of position in the hypothetical "aromatic" transition state of the thermal Cope rearrangement, designated "**a**" or active and "**n**" or nodal after the allyl radical, have concentrated on their effect in the "**n**" positions. In order to provide a quantitatively reliable reference for the "**a**" position, the activation parameters of the degenerate rearrangement of (6-^{13}C)-1,4-diphenylhexa-1,5-diene have been evaluated: E_a = 30.8 ± 0.4 kcal/mol; log A = 10.14 ± 0.2. The soundly energetically-based proposition that these observations relate to a concerted mechanism is strongly supported by the observation of a 3.0-fold increase in rate of approach to equilibrium on increasing the pressure from 1 bar to 6000 bar (162 °C; benzene-d_6). This rearrangement, like that of *cis*-1,2-divinylcyclobutane and *rac*- and *meso*-3,4-diphenylhexa-1,5-diene, has a negative volume of activation. In contrast, *trans*-1,2-divinylcyclobutane, which does not rearrange by a cyclic transition state and gives cycloocta-1,5-diene, 4-vinylcyclohexene, and butadiene as products, has a positive volume of activation. To place the possibility of reaction by the homolytic/colligative (dissociative/recombinative) mechanism on a "quantitative" base, a further sighting on the heat of formation of the cinnamyl radical is provided by activation parameters for thermal syn–anti equilibration between (*E*)- and (*Z*)-1,1′-bi-3-phenylcyclohex-2-enylidene: E_a = 35.8 ± 0.2 kcal/mol; log A = 12.7 ± 0.1. After correction for conjugative interaction between phenyl and the double bond in the educts and without regard for any proposed structure for the transition state, the two phenyl groups in "**a**" positions appear to have lowered the enthalpy of activation by 7.7 kcal/mol relative to the paradigm, hexa-1,5-diene, whereas the two phenyl groups in the "**n**" positions of 3,5-diphenylhexa-1,5-diene have lowered the enthalpy of activation by 17.0 kcal/mol.

Many changes have been rung on the Cope rearrangement in efforts to distinguish among various mechanistic hypotheses, including the concerted, the associative diradical, and the homolytic/colligative. Despite continuous experimental, theoretical, and synthetically applied interest in the Cope rearrangement, the effect of radical-stabilizing groups at the 1, 3, 4, and 6 positions of hexa-1,5-diene has not been examined as thoroughly as might have been expected.

Unlike benzene, the "aromatic", concerted transition state of the Cope rearrangement, no matter by whom formulated, formally has two types of position as indicated in Scheme 1: two of the "n" type corresponding to the nodal, "passive" position in an allyl radical and four of the "**a**" type corresponding to the substituent-sensitive, "active", pair of terminal positions of an allyl radical.[3] Despite the extraordinarily dramatic effects observed with oxide[4] and nitride[5] at an "**a**" position, more attention has been directed toward substituents in the "n" position.

Dewar[3] and Schmid[6] were the first to explore the use of radical-stabilizing substituents at the "**n**" positions to engineer a qualitative change in the rate-determining transition state from the widely accepted, concerted chair[7] (in the terms of Gajewski[8] and Borden[9]) toward that of an intramolecular, two-step, associative–dissociative passing over a cyclohexa-1,4-diyl diradical as intermediate, the "diyl" mechanism for short.[3,7] Since the pioneering work of Dewar, the phenyl group has been used so widely as the radical-stabilizing substituent that the practice is continued in this work, even though it would have been far preferable, in our opinion and, we presume, also in that of Borden,[9] if the lead of the late Hans Schmid and his co-workers[6] in employing the axially symmetrical cyano group rather than the discus-like phenyl group had been followed. The panoply of phenyl-substituted Cope rearrangements is displayed in Chart 1. Quantitative measures of the perturbations on enthalpy and entropy of activation are given in Table 1.[10–12]

As an example of perturbation by the phenyl group on "active" positions, 3,4-diphenylhexa-1,5-diene has been examined in a vain attempt to realize the homolytic/colligative mechanism passing over two kinetically free and in this instance phenyl-stabilized allyl (cinnamyl) radicals.[13] Other examples include

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[⊛] Abstract published in *Advance ACS Abstracts,* April 15, 1994.

[1] Harvard University.

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[3] Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* 1977, *99,* 4417–4424.

[4] Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975,** *97,* 4765–4766. Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978,** 3119–3121. Evans, D. A.; Nelson, D. A. M. *J. Am. Chem. Soc.* **1980,** *102,* 774–782.

[5] Sprules, T. J.; Galpin, J. D.; Macdonald, D. *Tetrahedron Lett.* **1993,** *34,* 247–250.

[6] Wehrli, R.; Schmid, H.; Belluš, D.; Hansen, H.-J. *Helv. Chim. Acta* **1977,** *60,* 1325–1356.

[7] Doering, W. v. E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971,** *27,* 5299–5306.

[8] Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1978,** *100,* 6268–6269. Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1978,** *100,* 6269–6270. Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979,** *101,* 6693–6704.

[9] Hrovat, D. A.; Borden, W. T.; Vance, R. L.; Randon, N. G.; Houk, K. N.; Morokuma, K. *J. Am. Chem. Soc.* **1990,** *112,* 2018–2019.

[10] Emrani, J. Ph.D. Dissertation, Indiana University, 1985 (Gajewski, J. J., research advisor); *Diss. Abstr. B* **1985,** *46,* 1922 (Order No. 85-16,636). The values given in Table 1 are our recalculation of Emrani's experimental data.

[11] Roth, W. R.; Lennartz, H.-W.; Doering, W. v. E.; Birladeanu, L.; Guyton, C. A.; Kitagawa, T. *J. Am. Chem. Soc.* **1990,** *112,* 1722–1732.

[12] Marvell, E. N.; Li, T. H.-c. *J. Am. Chem. Soc.* **1978,** *100,* 883–888.

Scheme 1

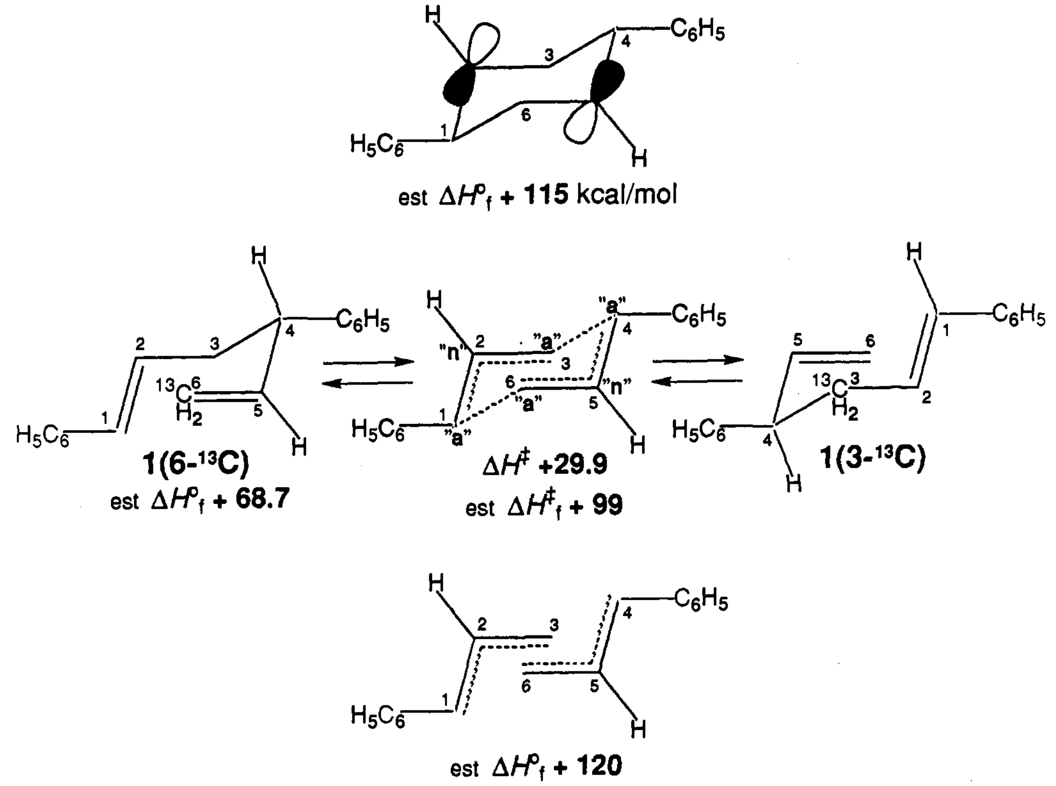
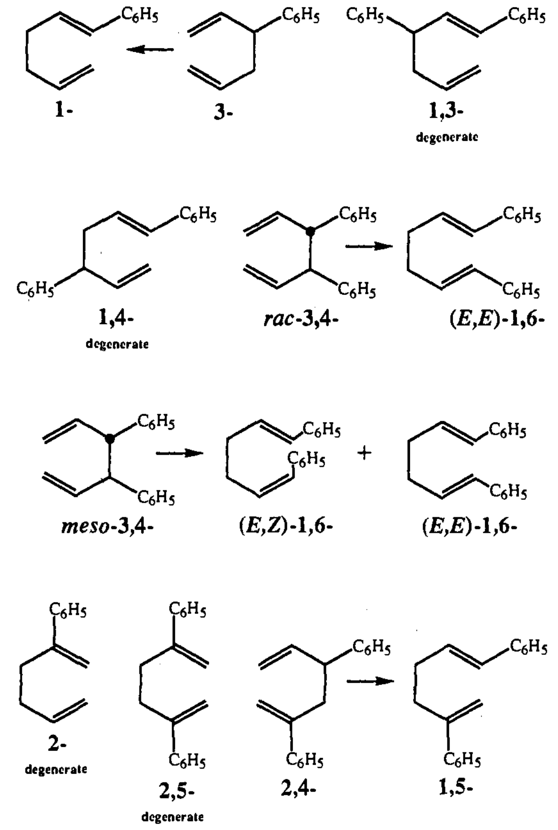


Chart 1



3-phenyl-,[3] 1,3-diphenyl-,[10] and 2,4-diphenylhexa-1,5-diene.[3] From all these examples, the effect of phenyl on "a" positions might have become clear, but each falls short in one way or another: 3-phenyl for involving only a single perturbation and showing a disturbingly large difference in activation parameters between gas phase and solution;[3] 1,3-diphenyl from substantial uncertainties in the Arrhenius parameters;[10] 3,4-diphenyl from a steric factor that may translate into a large, perhaps kinetically biasing, thermodynamic driving force;[13] and 2,4-diphenyl in combining effects at both the "a" and the "n" positions in a single compound.[3]

Table 1. Activation Parameters for Thermal Cope Rearrangements for Several Phenyl-Substituted Hexa-1,5-dienes Drawn in Chart 1

compd[a]	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]	T,[d] °C	ref
hexa-1,5-diene[e]	33.5 ± 0.5	−13.8 ± 1.0	232.7 ± 25.5	7
3-phenyl-[e,f]	31.5 ± 0.0	−12.4 ± 0.0	219.7 ± 29.8	3
3-phenyl-[f,g]	28.1 ± 0.4	−16.8 ± 1.0	182.7 ± 17.3	3
1,3-diphenyl-[h]	28.2 ± 0.7	−16.9 ± 3.0	170.8 ± 26.2	10
1,4-diphenyl-[i]	29.9 ± 0.2	−15.0 ± 0.4	175.0 ± 21.0	*p*
1,4-diphenyl-[h]	32.0 ± 1.9	−9.6 ± 4.3	185.3 ± 25.3	10
rac-3,4-diphenyl-[j,k]	24.0 ± 0.2	−12.4 ± 0.6	100.0 ± 10.0	13c
meso-3,4-diphenyl-[l,m]	27.7 ± 0.3	−12.4 ± 0.7	153.2 ± 20.5	13d
meso-3,4-diphenyl-[l,k]	29.0 ± 0.3	−10.0 ± 0.7	153.2 ± 20.5	13d
2-phenyl-[g]	29.3 ± 1.6	−9.9 ± 3.6	160.0 ± 10.0	3, 12
2,5-diphenyl-[g,o]	21.2	−20.8	91.6 ± 9.4	3
2,5-diphenyl-[i]	21.3 ± 0.2	−20.8 ± 0.5	83.1 ± 24.7	11
2,4-diphenyl-[g,n]	24.6 ± 0.8	−16.9 ± 0.7	140.0 ± 20.0	3

[a] All compounds are hexa-1,5-dienes and their rearrangements are degenerate except where otherwise noted. [b] In kcal/mol. [c] In cal mol^{-1} K^{-1} (eu). [d] Temperature range over which kinetic measurements were made. [e] Gas phase. [f] Product is 1-phenylhexa-1,5-diene. [g] In *o*-dichlorobenzene. [h] In hexachlorobutadiene. [i] In benzene-d_6. [j] In *n*-heptane. [k] Product is (*E*,*E*)-1,6-diphenylhexa-1,5-diene. [l] In *n*-hexane. [m] Product is (*E*,*Z*)-1,6-diphenylhexa-1,5-diene. [n] Product is 1,5-diphenylhexa-1,5-diene. [o] Two temperatures: no estimate of uncertainty. [p] This work.

1,4-Diphenylhexa-1,5-diene seems a natural choice for focusing on the effect of phenyl in "a" positions. Placement of the two phenyl groups in identical environments has the advantage of amplifying by a factor of 2 whatever effect a phenyl group may exercise. In fact, this compound, labeled with deuterium, has already been the subject of a prior investigation,[10] in which rates

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(13) (a) Koch, H. P. *J. Chem. Soc.* **1948**, 1111–1117. (b) Lutz, R. P.; Bernal, S.; Boggio, R. J.; Harris, R. O.; McNicholas, M. W. *J. Am. Chem. Soc.* **1971**, *93*, 3985–3990. (c) Lutz, R. P.; Berg, H. A. J. *J. Org. Chem.* **1980**, *45*, 3915–3916. (d) Diedrich, M. K.; Hochstrate, D.; Klärner, F.-G.; Zimny, B. *Angew. Chem., Int. Ed. Engl.* In press.

Table 2. Specific Rate Constants and Activation Parameters for the Thermal Isomerization of (6-^{13}C)-1,4-diphenylhexa-1,5-diene {**1**(6-^{13}C)} to (3-^{13}C)-1,4-diphenylhexa-1,5-diene {**1**(3-^{13}C)} in Benzene-d_6

T, °C	k_1,[a] × 10^{-6} s^{-1}	K
154.0 ± 0.2[b]	2.54 ± 0.02	1.00 ± 0.01
165.2 ± 0.3[b]	6.33 ± 0.08	1.00 ± 0.03
186.0 ± 0.2[b]	31.3 ± 0.3	1.00 ± 0.02
196.0 ± 0.1[b]	65.4 ± 0.5	1.00 ± 0.02
196.0 ± 0.1[c]	64.9 ± 1.1	1.00 ± 0.03
196.0 ± 0.1[d]	65.5 ± 0.7	1.00 ± 0.00

Arrhenius Plot [$1/T$ vs log k]
E_a = 30.75 ± 0.39 kcal/mol[e]
log A = 10.14 ± 0.19[e]

Eyring Parameters
ΔH^* = 29.9 ± 0.19 kcal/mol[e]
ΔS^* = −15.0 ± 0.8 eu[e]

[a] Calculated by linear regression using the usual expression for reversible first-order reaction: $(k_1 + k_{-1}) = (1/t)\ln[(X_{eq} - X_0)/(X_{eq} - X)]$; $K = k_{-1}/k_1$. [b] 0.1 M solution, 0.0047 M in 18-crown-6 ether. [c] 0.05 M solution, 0.0036 M in 18-crown-6 ether and 0.001 M in dihydroanthracene. [d] 0.05 M solution, 0.0036 M in 18-crown-6 ether. [e] 95% confidence limits. [f] Calculated at 175.0 °C.

of rearrangement at various temperatures have been measured and Arrhenius parameters determined, but with insufficient accuracy to satisfy the purpose of the present study. In this work, the degeneracy of the rearrangement is broken by ^{13}C, a negligible perturbation on the thermochemistry and kinetics.

The selected compound, (6-^{13}C)-1,4-diphenylhexa-1,5-diene, is synthesized in the unexceptional manner described in the Experimental Section. Rates of its degenerate rearrangement in benzene-d_6 are followed by ^{1}H NMR at four temperatures in the range 154–196 °C. The primary data are offered in Table SI as supplementary material, while the derived rate constants and activation parameters are given in Table 2. The complete absence of products expected of reaction by the homolytic/colligative mechanism, such as 1,6-diphenylhexa-1,5-diene, supports the contention that the reaction under study is of the concerted Cope type.

To gain further support for this assumption, the effect of pressure on several potential Cope rearrangements has been examined. If one expands the concept, which stems from the temperature dependence of competing single step and multistep cycloadditions, that the volumes of activation of cyclic transition states are smaller as a consequence of their greater packing fractions than those of corresponding acyclic transition states,[14] then one expects of the Cope rearrangement of hexa-1,5-diene by way of its concerted pericyclic transition state a negative volume of activation and therewith an acceleration of rate by increased pressure.[13d] A similarly negative volume of activation is also expected of a diradical process, provided an intermediate cyclohex-1,4-diyl represents the rate-determining transition state. However, were a homolytic/colligative mechanism involved, a positive volume of activation and a deceleration of rate in response to an increase in pressure would be anticipated.

As a test case for this hypothesis, *cis*- and *trans*-1,2-divinylcyclobutanes (***cis*-2** and ***trans*-2**) have been selected as a model system (Scheme 2).[15] For geometrical reasons, only ***cis*-2** can rearrange to cycloocta-1,5-diene by a pericyclic, concerted Cope mechanism, whereas ***trans*-2** requires initial homolysis of the C1–C2 bond as a prelude to rearrangement and cleavage. In fact, an increase in pressure from 1 bar to 6 kbar leads to an increase in rate of rearrangement of ***cis*-2** to **3** by a factor of 4.5. From the pressure dependencies of the rate constants at 69.8 °C in Table 3, an activation volume, $\Delta V^{\ddagger} = -(13.4 \pm 0.6)$ cm^3/mol, can be calculated, which is in full accord with the formation of a new ring in the transition state. In contrast, the reaction of ***trans*-2** to **3**, **4**, and **5** is slowed by pressure and the volume of activation becomes positive: $\Delta V^{\ddagger} = +(4.2 \pm 0.6)$ cm^3/mol, consistent with the hypothesis of a diradical mechanism. Because the product ratios, [**3**]:[**4**]:[**5**],[16] show no significant pressure dependence, the activation volumes of the individual reactions are essentially equal. These values are calculated from the pressure-dependent rate constants given in Table 4 and are shown in Scheme 2. It is concluded that neither ring closure of the diradical to **3** or **4** nor cleavage to **5** are product determining. Had that not been the case, differing volumes of activation would have been expected. Quite probably pressure-independent rotations about the C–C bond in the diradicals **6** determine the distributions among the three products.

It is also of interest to compare the volumes of reaction that can be determined from the partial molar volumes (V) (Scheme 2) in the rearrangements of ***trans*-2** to **4** (ΔV^R = −9.6 cm^3/mol) and ***trans*-2** to **3** (ΔV^R = −17.4 cm^3/mol) in which six- and eight-

Scheme 2

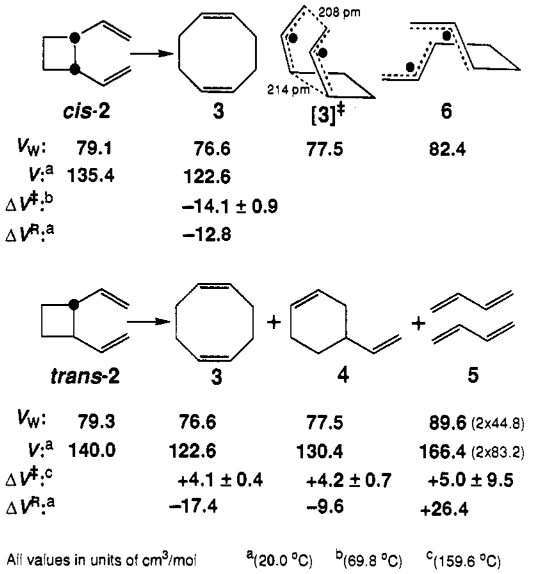

Table 3. Pressure Dependence of the Specific Rate Constants of the Rearrangement of ***cis*-2** to **3** at 69.8 °C in n-Heptane

p, bar	k_1, ×10^{-5} s^{-1}	p, bar	k_1, ×10^{-5} s^{-1}
200	3.44 ± 0.18	1000	5.08 ± 0.13
400	3.78 ± 0.10	1500	5.65 ± 0.06
600	4.16 ± 0.33	2000	6.54 ± 0.12
800	4.64 ± 0.14	3000	8.53 ± 0.21

Table 4. Pressure Dependence of the Specific Rate Constants of the Conversions of ***trans*-2** to **3**, **4**, and **5** at 159.6 °C in n-Heptane

p, bar	$\sum k_1$[a,b]	k_1[a,c]	k_1[a,d]	k_1[a,e]
200	2.71 ± 0.08	1.87 ± 0.07	0.754 ± 0.071	0.088 ± 0.041
400	2.58 ± 0.06	1.74 ± 0.05	0.728 ± 0.053	0.113 ± 0.031
600	2.56 ± 0.06	1.69 ± 0.05	0.705 ± 0.053	0.172 ± 0.031
800	2.54 ± 0.05	1.70 ± 0.04	0.687 ± 0.038	0.147 ± 0.022
1000	2.50 ± 0.05	1.67 ± 0.04	0.677 ± 0.039	0.150 ± 0.022
1300	2.43 ± 0.04	1.63 ± 0.03	0.671 ± 0.034	0.136 ± 0.019
2000	2.18 ± 0.03	1.46 ± 0.02	0.607 ± 0.022	0.116 ± 0.013
3000	1.93 ± 0.03	1.31 ± 0.03	0.541 ± 0.027	0.076 ± 0.016

[a] In units of 10^{-5} s^{-1}. [b] Over-all rate constant. [c] k_1(***trans*-2**→**4**). [d] k_1(***trans*-2**→**3**). [e] k_1(***trans*-2**→**5**).

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(14) Klärner, F.-G. *Chem. Z.* **1983**, *23*, 53–63. Klärner, F.-G.; Krawczyk, B.; Ruster, V.; Deiters, U. V. *J. Am. Chem. Soc.* Submitted for publication.

(15) Hammond, G. S.; De Boer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899–902.

(16) A quantitative analysis of butadiene was not possible because of its volatility. Nonetheless the amount of butadiene is estimated, as described in detail in the experimental section, as a loss of C_8H_{12} isomers against n-nonane as internal standard. This estimate being significantly less accurate than that of the C_8H_{12} isomers, the activation volume for the rearrangement of ***trans*-2** to **5** has the greatest uncertainty.

Table 5. Pressure Dependence of Specific Rate Constants of the Equilibration **1**(6-^{13}C) ⇄ **1**(3-^{13}C) at 162.0 °C in Benzene-d_6

p, bar	t, min	ratio[a]	k_1[b]
1	1000	76.4:23.6	5.31
530	1093	72.1:27.9	6.23
1000	1090	70.3:29.7	6.88
1530	1080	68.1:31.9	7.86
2020	1085	65.7:34.3	8.87
2530	1088	64.8:35.2	9.33
3010	1080	63.1:36.9	10.3
3520	1080	61.5:38.5	11.3
6000	1000	57.9:42.1	15.3

[a] The ratio of **1**(6-^{13}C) to **1**(3-^{13}c) as measured by ^{1}H NMR after time of reaction (t). [b] In units of 10^{-6} s^{-1}.

membered rings, respectively, are formed at the expense of a four-membered ring. This observation that the volume requirement in the ring enlargement from four to six members is much less than it is in that of four to eight members makes it likely that the volume of activation depends not only on the number[13d] but also on the size of the newly forming ring. The van der Waals volumes (V_W)[17,18] and the intrinsic volumes of the ground and transition states of the C_8H_{12} isomers shown in Scheme 2 do not differ from each other appreciably and cannot explain the observed differences in volumes of activation and reaction.

In analogy to the rearrangement of ***cis*-2** to **3**, the degenerate rearrangement of 1,4-diphenylhexa-1,5-diene reveals an acceleration in rate of approach to equilibrium between **1**(6-^{13}C) and **1**(3-^{13}C) in response to an increase in pressure from 1 bar to 6 kbar by a factor of 3.0. The volume of activation is calculated to be $\Delta V^* = -(9.1 \pm 0.5)$ cm^3/mol from the pressure dependence of the specific rate constants at 162 °C given in Table 5. This value is similar to those found in the rearrangement of *meso*-3,4-diphenylhexa-1,5-diene to (*E*,*Z*)-1,6-diphenylhexa-1,5-diene (127.5 °C: $\Delta V^* = -(13.3 \pm 0.3)$ cm^3/mol) and to (*Z*,*Z*)-1,6-diphenylhexa-1,5-diene (127.5 °C: $\Delta V^* = -(8.8 \pm 0.2)$ cm^3/mol).[13d] The rate acceleration established here for the interconversion of **1**(6-^{13}C) and **1**(3-^{13}C) argues strongly for the pericyclic mechanism.

The observed enthalpy of activation of the degenerate rearrangement of **1**, $\Delta H^* = 29.9$ kcal/mol, is lower than that of unsubstituted hexa-1,5-diene, $\Delta H^* = 33.5$ kcal/mol, by 3.6 kcal/mol.[19] Without correction for the stabilizing conjugative interaction in the single styrene moiety of the educt, this difference cannot be equated with the magnitude of the perturbation on the transition state. Knowledge of the conjugative interaction between a double bond and a phenyl group is the critical element. Perhaps surprisingly, the magnitude of this factor is not known with great confidence because of the paucity of relevant thermochemical data in the literature.[20,21] An estimate of 4.1 kcal/mol can be made.[22] If this value is added to the enthalpy of activation of the Cope rearrangement of hexa-1,5-diene (33.5 kcal/mol, gas phase) as an apposite model corrected for stabilization by conjugative interaction in the educt, the observed enthalpy of activation of 1,4-diphenylhexa-1,5-diene, 29.9 kcal/mol, translates to a lowering of 7.7 kcal/mol in the enthalpy of formation of the transition state. Each phenyl group in an "**a**" position has thus appeared to stabilize the transition state by 3.9 kcal/mol.

Similar analysis of 2,5-diphenylhexa-1,5-diene, in which the substituents occupy "**n**" positions, reveals a lowering in enthalpy of formation of the rate-determining transition state of 17.0 kcal/mol (33.5[7] + 2(2.4)[23] − 21.3[11]), corresponding to 8.5 kcal/mol per phenyl group. If the conceptual scheme behind this analysis posits both 1,4- and 2,5-diphenylhexa-1,5-diene to proceed by a concerted mechanism, a phenyl group in an "n" position is more than twice as effective as one in an "**a**" position. If the transition state for the Cope rearrangement resembled that for dissociation to two allyl radicals, this result would be difficult to reconcile with the finding that the bond dissociation energy of 2,5-divinylhexa-1,5-diene (to a pair of 2-vinylallyl radicals)[24] is unchanged from that of unsubstituted hexa-1,5-diene;[25] that is, a vinyl group in the "**n**" position of the free allyl radical has no more effect here than it does on the two double bonds in the educt.

The effect of the phenyl groups in the 1- and 4-positions may be analyzed under an alternative hypothetical scheme, in which 1,6 bond-making precedes 3,4 bond-breaking, leading to the "diyl", 1,4-cyclohexadiyl diradical as intermediate. As the unsubstituted model for this comparison, a heat of formation for the cyclohexa-1,4-diyl diradical, by its very definition noninteractive, may be constructed from the heat of formation of cyclohexane (−29.5 kcal/mol)[21] by addition of twice the difference in heat of formation of propane and isopropyl radical (+46.3 kcal/mol).[26] The resulting estimate of +63.1 kcal/mol is 9.5 kcal/mol higher than the experimental heat of formation of the rate-determining transition state for the concerted Cope rearrangement [+53.6 kcal/mol: the heat of formation of hexa-1,5-diene (20.1 kcal/mol)[21] plus the enthalpy of activation (33.5 kcal/mol)[7]]. In other words, the energy of concert[27,28] of the rearrangement of hexa-1,5-diene *vis-à-vis* the "diyl" as model is 9.5 kcal/mol.

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(17) The van der Waals volumes (V_W) are the intrinsic volumes of the ground and transition states multiplied by Avogadro's number. They are calculated by a computer program MOLVOL developed by U. Artschwager-Perl and D. Oebels, a copy of which can be obtained on request. This program employs Cartesian coordinates derived from molecular or quantum mechanical calculations and atomic van der Waals radii (R_W) derived by crystallographic analysis (R_W(C) = 1.80 Å; R_W(H) = 1.17 Å).

(18) (a) Artschwager-Perl, U. Dissertation, Ruhr-Universität Bochum, 1989. (b) Yoshimura, Y.; Osugi, J.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 680–683. (c) Asano, T.; Le Noble, T. J. *Rev. Phys. Chem. Jpn.* **1973**, *43*, 82–91.

(19) However, note well that the datum from hexa-1,5-diene relates to the gas phase[7,12] whereas that from 1,4-diphenylhexa-1,5-diene refers to reaction in solution in benzene. The difference in phase might be ignored were it not for the observation by Dewar and Wade[3] in the rearrangement of 3-phenyl-1,5-hexadiene of a difference of 3.4 kcal/mol between the gas ($\Delta H^* = 33.5$ kcal/mol) and the liquid ($\Delta H^* = 30.1$ kcal/mol) phase (see Table 1) (4-fold difference in rate).[12] Were this correction applied, the apparent difference in enthalpy of activation between 1,4-diphenyl-substituted and unsubstituted 1,5-hexadiene would vanish.

(20) Included in the collection of Pedley, Naylor, and Kirby[21] are heats of formation of styrene (35.35 kcal/mol) and indene (39.05 kcal/mol) and heats of combustion (liquid only) of 2-phenylpropene, 1,2-dihydronaphthalene, 1-phenylcyclohexene, and *cis*- and *trans*-1-phenyl-3,3-dimethylbut-1-ene.

(21) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(22) The difference between the known heats of formation of ethene and styrene is 22.8 kcal/mol.[21] This value is taken for $\Delta\Delta H^\circ_f$[RCH=CH$_2$/RCH=CH(C$_6$H$_5$)] and has also been incorporated as general in storage schemes like Benson's or Allinger's MM. Applied to propene, $\Delta H^\circ_f = +4.78$ kcal/mol, an estimate of the experimentally unknown heat of formation of 1-phenylpropene of +27.6 kcal/mol is generated. Subtraction from the heat of formation of 1-phenylpropane (+1.9 kcal/mol) affords an estimated heat of hydrogenation of 25.7 kcal/mol. This value is lower than the heats of hydrogenation of monoalkyl substituted olefins, including that of propene (−29.8 kcal/mol), by 4.1 kcal/mol. This is the value we currently take for the conjugative interaction of phenyl in compounds of the type *trans*-RCH=CH(C$_6$H$_5$), but with some reservation! Note that any differences in steric factors are absorbed into "conjugative interaction", despite the electronic component alone being relevant to the argument.

(23) A heat of hydrogenation of 2-phenylpropene, estimated to be −27.4 kcal/mol (from a heat of formation of 2-phenylpropene, itself estimated on the basis of footnote 23 in ref 11 to be 28.4 kcal/mol, and a known heat of formation of 2-phenylpropane[21]), is 2.4 kcal/mol less than that of RCH=CH$_2$ and is taken as the value for conjugative interaction in olefins of the type RC(C$_6$H$_5$)=CH$_2$.

(24) Roth, W. R.; Staemmler, V.; Neumann, M.; Schmuck, C. *Chem. Ber.* In press.

(25) Doering, W. v. E.; Roth, W. R.; Bauer, F.; Boenke, M.; Breuckmann, R.; Ruhkamp, J.; Wortmann, O. *Chem. Ber.* **1991**, *124*, 1461–1470.

(26) (a) Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347–1353. (b) Seakins, P. W.; Pilling, M. J.; Niiranen, J. T.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847–9855.

(27) "Energy of concert" translates awkwardly and ambiguously into German; Professor Roth uses the term, "Übergangzustands-Resonanzenergie".[28]

(28) Doering, W. v. E.; Roth, W. R.; Bauer, F.; Breuckmann, R.; Figge, L.; Lennartz, H.-W.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.* **1988**, *121*, 1–9.

Analysis of 1,4-diphenylhexa-1,5-diene proceeds analogously. Its heat of formation is estimated from that of hexa-1,5-diene by the addition of +22.8 kcal/mol[22] and +25.70 kcal/mol.[29] To the resulting estimated heat of formation (+68.7 kcal/mol), addition of the enthalpy of activation (+29.9 kcal/mol) leads to an estimated heat of formation of the rate-determining transition state of +98.6 kcal/mol. Estimation of the heat of formation of a noninteractive, 2,5-diphenylcyclohexa-1,4-diyl diradical, which shall serve as the non-concerted model in this analysis, is derived by replacing two of the methylene groups in the cyclohexa-1,4-diyl diradical (+63.1 kcal/mol) by two benzyl groups (2 × 25.7 kcal/mol). From the resulting heat of formation, +114.5 kcal/mol, an energy of concert of 15.9 kcal/mol is estimated. This value, being greater than that of the paradigm by 6.4 kcal/mol, is consistent with each phenyl group having stabilized the actual transition state, which is presumed to be that involved in the concerted mechanism, by 3.2 kcal/mol. The mean of the magnitude of the perturbation by the two analyses is 3.5 kcal/mol.

An identical analysis of 2,5-diphenylhexa-1,5-diene leads to an essentially zero energy of concert *vis-à-vis* 1,4-diphenylcyclohexa-1,4-diyl as the defined model.[11] In a future publication,[24] Roth and co-workers will indicate as weaknesses in this analysis its neglect of changes in steric energy associated with coplanarization of the phenyl group in the delocalized diyl and its acceptance of 13.0 kcal/mol as the delocalization energy of the benzyl radical instead of the now preferable value of 10.5 kcal/mol.[30] Bearing witness to an inevitable reliance on currently available thermochemical data, which is the experimental complement to current inadequacies of theoretical calculations on large molecules, as the weakness in all these analyses, they will draw a conclusion opposed to the earlier one.[11]

The homolytic/colligative mechanism has consistently seemed quite untenable for the unsubstituted paradigm, but now that the enthalpy of activation for cleavage of hexa-1,5-diene to two allyl radicals has been demonstrated by Roth and co-workers to be 55.7 kcal/mol,[31] reaction by this mechanism is seen to lie some 22 kcal/mol above the experimental value for its Cope rearrangement.[7] That it might have become tenable for 1,4-diphenylhexa-1,5-diene has already been proposed and rejected within the limitations of a poorly defined heat of formation of the cinnamyl radical.[32]

In the meantime, a value for the stabilization energy of the cinnamyl radical of 17.4 kcal/mol based on work of M. Herbold has been reported by Roth et al.[24] and another value is derived by addition of the increment of +5.4 kcal/mol above the stabilization energy of the benzyl radical proposed by Robaugh and Stein.[33] When added to the recent value for the stabilization energy of benzyl radical, 10.5 kcal/mol, advanced by Hippler and Troe,[30] a stabilization energy of 15.6 kcal/mol for cinnamyl results. To these, we now add a value based on the application of the method of thermal cis,trans isomerization about a double bond.[34,35]

Chart 2

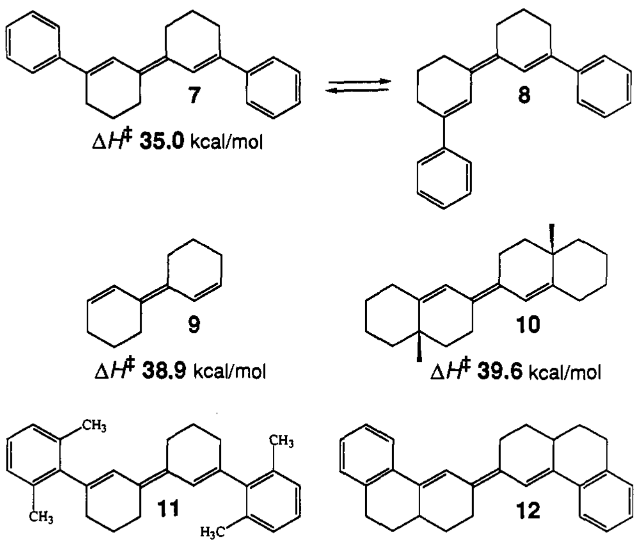

Table 6. Specific Rate and Equilibrium Constants and Activation Parameters for the Thermal Interconversion of (*E*)- (**7**) and (*Z*)-1,1′-Bi-3-phenylcyclohex-2-enylidene (**8**) in Benzene-d_6

T, °C	k_1,[a,b] $\times 10^{-6}$ s^{-1}	K
154.0 ± 0.2	2.22 ± 0.03	0.560
154.1 ± 0.2	2.11 ± 0.01	0.576
165.1 ± 0.2	6.12 ± 0.03	0.580
165.2 ± 0.2	6.08 ± 0.14	0.584
177.1 ± 0.2	18.36 ± 0.57	0.590
177.1 ± 0.2	18.36 ± 0.28	0.603
185.5 ± 0.3	39.50 ± 0.68	0.610
185.9 ± 0.3	41.89 ± 1.28	0.585
196.2 ± 0.2	91.32 ± 1.35	0.610
196.3 ± 0.2	95.06 ± 1.63	0.619

Arrhenius Plot [$1/T$ vs log k]
$E_a = 35.84 \pm 0.19$ kcal/mol
log $A = 12.66 \pm 0.09$

Eyring Parameters[c]
$\Delta H^{\ddagger} = 35.0 \pm 0.2$ kcal/mol
$\Delta S^{\ddagger} = -3.4 \pm 0.4$ eu

Thermodynamics [$1/T$ vs log K]
$\Delta H^{\circ} = 0.67 \pm 0.09$ kcal/mol
$\Delta S^{\circ} = 0.46 \pm 0.21$ eu

[a] Calculated by linear regression using the usual expression for reversible first-order reaction: $(k_1 + k_{-1}) = (1/t)\ln[(X_{eq} - X_0)/(X_{eq} - X)]$; $K = k_{-1}/k_1$. [b] Double all standard errors for 90% confidence limits. [c] Calculated at 175.2 °C.

Selection of bi-3-phenylcyclohex-2-enylidenes, **7** and **8**, as the substrate is motivated in large measure by its closeness in structure to the reference trienes **9** and **10** in Chart 2. Synthesis and isolation of 7 in pure form is described in the Experimental Section. Thermal isomerization is effected in solution in benzene-d_6 at temperatures ranging from 154 to 196 °C. From the primary data, available as supplementary material in Table SII, specific rate constants and activation parameters are calculated and recorded in Table 6. The enthalpy of activation for conversion of **7** to **8** is 35.0 kcal/mol. This value may be compared with that of 38.9 kcal/mol for **9**[35a] and 39.6 kcal/mol for **10**[36] in Chart 2. If stabilization energy is defined strictly as illustrated for the least substituted cases in Chart 3, that is, in neglect of styrene conjugative interaction, stabilization by cinnamyl is 2.2 kcal/mol greater than that by allyl (13.5 kcal/mol), or 15.7 kcal/mol in good agreement with the value offered by Robaugh and Stein (10.5[30] + 5.4[33]). A heat of formation of the cinnamyl radical can then be derived: estimated heat of formation of *trans*-1-phenylpropene (+4.5 + 22.8[22] = 27.6) + 48.3[26] − 15.7 = 60.2 or 120.4 kcal/mol for two cinnamyl radicals. The estimated heat of formation of the transition state of the Cope rearrangement of 1,4-diphenylhexa-1,5-diene being 98.6 kcal/mol, energy of concert *vis-à-vis* the homolytic/colligative mechanism is estimated

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(29) See footnote 22 in ref 11: the difference in heat of formation of an aliphatic methylene group and an alkyl disubstituted benzyl group.

(30) Hippler, H.; Troe, J. *J. Phys. Chem.* **1990**, *94*, 3803–3806.

(31) Roth, W. R.; Bauer, F.; Beitat, A.; Ebbrecht, T.; Wüstefeld, M. *Chem. Ber.* **1991**, *124*, 1453–1460.

(32) See particularly, p 1729 of ref 11.

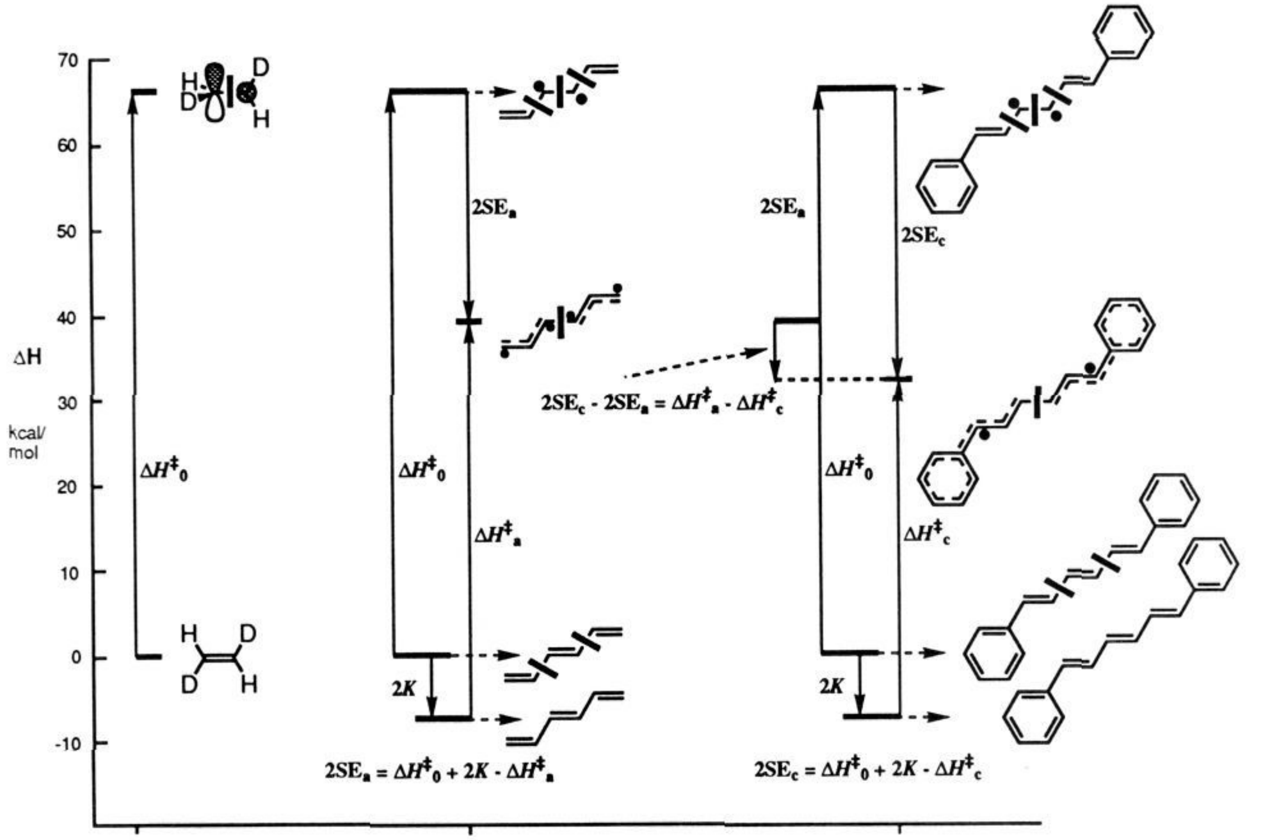
(33) Robaugh, D. A.; Stein, S. E. *J. Am. Chem. Soc.* **1986**, *108*, 3224–3229.

(34) Doering, W. v. E.; Beasley, G. H. *Tetrahedron* **1973**, 2231–2243.

(35) (a) Doering, W. v. E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 4288–4297. (b) Doering, W. von E.; Sarma, K. *J. Am. Chem. Soc.* **1992**, *114*, 6038–6043.

(36) Doering, W. v. E.; Shi, Y.-q; Zhao, D.-c. *J. Am. Chem. Soc.* **1992**, *114*, 10763–10766.

Chart 3



K = The Kistiakowsky: The unit of enthalpy of conjugation in polyenes (3.74 kcal/mol)

to be some 22 kcal/mol, a value far outside conservative estimates of uncertainty.

Nonetheless, the possibility has been considered that homolysis could generate cinnamyl radicals in low steady state concentration and initiate a chain process, involving addition followed by internal rotation and elimination of a chain-propagating cinnamyl radical. In order to probe this possibility, **1**(^{12}C) is heated at 154 °C in thiophenol as solvent. With the exception of one product of *m/e* 153 (addition of thiophenol to a phenylpropene leads to *m/e* 228), all other products separable by GC have *m/e* 344, corresponding to an addition of thiophenol to educt, which apparently occurs more rapidly than the Cope rearrangement.

At the much higher temperature of 259 °C in the presence of 9,10-dihydroanthracene as radical trapping agent, (*E,E*)- and (*E,Z*)-1,6-diphenylhexa-1,5-diene and phenylpropenes (mainly *trans*-1- but also some *cis*-1- and 3-phenylpropene) appear in substantial amount. Although colligation of two cinnamyl radicals can generate all the isomers of 1,6-, 1,4-, and 3,4-diphenylhexa-1,5-dienes in principle, in practice neither of the 3,4-diphenyl isomers is seen owing to an unfavorable thermochemistry, which causes (*E,E*)- and (*E,Z*)-1,6-diphenylhexa-1,5-diene to be the only products of the rearrangement of 3,4-diphenyl at lower temperatures.[13b,d] Strong evidence for the incursion of the homolytic/colligative mechanism is given by the formation in substantial amount of the phenylpropenes, consistent with the product of hydrogen atom transfer by 9,10-dihydroanthracene (see Table 7). Although these experiments could not be conducted with sufficient accuracy or reproducibility to provide reliable activation paameters, they are nonetheless in accord with the generation of cinnamyl radicals at high temperature, if by no means definitive in establishing the homolytic/colligative mechanism.

A cautionary comment about the quantitative reliability of certain of the conclusions in this paper notes the surprisingly small number of thermochemical data in the literature relating to the phenyl group. In light of the ultimate goal of chemistry—the translation of structure of educts and products into rates of interconversion and positions of equilibria—it is hard to excuse the continuing neglect of thermochemistry. Had this work and others been carried out with cyano in place of phenyl, the situation would have been no better. Further to emphasize the gratuitous complications that have been introduced by the choice of phenyl as a π-electron interacting group, we note that three possibly useful definitions of conjugative interaction between phenyl and olefin and three of stabilization enthalpy in the cinnamyl radical can be considered in principle: one in which the plane of phenyl is perpendicular to the plane occupied by interacting olefin; a second in which a coplanar relation exists; and a third in which the most favorable balance is struck between delocalization energy and steric energy at some intermediate angle. We conclude that a proper study of phenyl in this and probably other situations requires examination also of compounds like **11** and **12** in Chart 2.

Table 7. The Results (in %) of Heating (*E*)-1,4-Diphenyl-(^{12}-C)-hexa-1,5-diene (**1**) at 259 °C in Toluene in the Presence of 9,10-Dihydroanthracene

products	0.0 h	1.5 h	3.0 h	6.0 h	24 h
3-PP[a,c]		3.7	6.8	10.4	11.7
(*Z*)-1-PP		1.4	2.7	4.1	6.4
(*E*)-1-PP		15.8	27.4	40.8	54.8
(*Z*)-1,4-DPH[b]		7.5	4.4	2.0	
(*E*)-1,4-DPH	>99.9	67.4	41.8	21.8	10.9
(*E,Z*)-1,6-DPH		1.2	3.6	4.2	3.3
(*E,E*)-1,6-DPH		3.0	13.3	16.7	12.9

[a] Phenylpropene. [b] Diphenylhexa-1,5-diene. [c] Although concentrations of these compounds are normalized to 100%, other products, including higher oligomers, are omitted.

W.v.E.D. belatedly takes an opportunity to accept the evidence for the irreproducibility of the alleged realization of "The Carbon Analogue of the Claisen Rearrangement of Phenyl Allyl Ether"[37] and apologizes to those whose careful work has made the case.[38,39]

Experimental Section

General Methods. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.8 MHz; C_6D_6) spectra are recorded on a Brucker AM-500 instrument. Chemical shifts are reported in ppm (δ) relative to TMS. Infrared spectra (cm^{-1}) are recorded on a Perkin-Elmer Model 337 grating spectrophotometer. Analytical GLC is effected on a Hewlett-Packard 5890A instrument with a Hewlett-Packard recorder-digital integrator HP 3393A; column A, 7% cyanopropyl–7% phenylpolysiloxane (J & W Scientific, DB 1701), 0.53 mm i.d. × 30 m operated at oven temperature 100–180 °C, He 10 lb; column B, 100% methylpolysiloxane (J & W Scientific, DB1), 0.53 mm i.d. × 30 m.

In the high-pressure investigations, ^{1}H NMR (300 MHz) spectra are recorded on a Brucker AMX-300 instrument. Analytical GLC is effected on a Hewlett-Packard 5890 instrument with a Shimadzu recorder digital integrator C-R3A (column C, silicon oil OV 1701 on fused silica (25 m) operated at oven temperature 70 °C, He). For pressure-dependent kinetic measurements, a 7-kilobar vessel is heated by an external oil bath thermostated to ±0.2 °C and pressurized by a hand-driven press (Nova-Swiss). In order to follow the time dependence of a reaction at elevated pressure, one exit of the vessel is connected to a valve having a fine spindle, which allows the release of a small sample (ca. 100 μL) from the pressurized reaction mixture (10 mL). The released samples are analyzed by GC (column C). For measurements of densities a Densimeter DMA (Chempro) is used.

***trans*-4-Cyano-1,4-diphenylbutene-1.** *trans*-Cinnamyl chloride (Aldrich; NMR consistent with pure trans; 19.8 g, 0.130 mol) is slowly added at 45 °C under argon to a stirred mixture of phenylacetonitrile (Aldrich; 17.45 g, 0.149 mol), 50% NaOH (46 mL), and benzyltriethylammonium chloride (2 g). Stirring at this temperature is continued for 4 h and then at room temperature overnight. The reaction mixture is treated with 100 mL of benzene and 175 mL of water. The separated organic layer is dried ($MgSO_4$) and concentrated *in vacuo*. Distillation of the residue (bp 162–164 °C at 0.5 mmHg) gives 10.6 g (36%) of *trans*-4-cyano-1,4-diphenylbutene-1, which crystallizes on standing at 0 °C. Recrystallization from MeOH gives pure nitrile: mp 45.5–46 °C; IR 2220; ^{1}H NMR ($CDCl_3$) 7.43–7.26 (m, 10 H), 6.52 (d, 1 H, J = 15.6 Hz), 6.19 (dt, 1 H, J = 15.6 Hz, J = 7.3 Hz), 3.94 (t, 1 H, J = 6.7 Hz), 2.87–2.77 (m, 2 H).

(*E*)-2,5-Diphenylpent-4-enal. A 1 M solution of diisobutylaluminum hydride (DIBAL) in toluene (Aldrich; 10 mL, 20% molar excess) is added to a stirred solution of *trans*-4-cyano-1,4-diphenylbutene-1 (3 g, 0.013 mol) in benzene at 40 °C under argon over a period of 60 min. Stirring is continued at this temperature for an additional 2 h and then overnight at room temperature. The reaction mixture is quenched with MeOH and water. The organic layer is washed twice with 5% sulfuric acid, water, aqueous $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated *in vacuo*. The crude reaction product (2.7 g) is purified by flash chromatography on silicagel (elution with 15% ether in hexane) to give 1.1 g (33%) of pure aldehyde: IR 1725; ^{1}H NMR ($CDCl_3$) 9.78 (d, 1 H, J = 0.2 Hz), 7.10–7.5 (m, 10 H), 6.40–6.48 (d, 1 H, J = 15.8 Hz), 6.08–6.18 (dt, 1 H, J = 15.8 Hz, J = 7.15 Hz), 3.67–3.75 (t, 1 H, J = 7.5 Hz), 2.98–3.08 (ddd, J = 7.5 Hz, J = 7.15 Hz, J = 7.8 Hz), 2.62–2.72 (ddd, 1 H, J = 7.5 Hz, J = 7.15 Hz, J = 7.8 Hz); ^{13}C NMR 199.88, 137.11, 135.62, 132.24, 129.02, 128.80, 128.37, 127.61, 127.12, 126.50, 125.98, 59.03, 33.23.

(*E*)-1,4-Diphenyl(1-^{13}C)hexa-1,5-diene. A solution of the aldehyde above (0.432 g, 1.53 mmol) in 5 mL of dry THF is added dropwise at 0 °C to a stirred solution of triphenyl-^{13}C-phosphonium ylide prepared from triphenyl(^{13}C)methylphosphonium iodide (0.9 g, 2.23 mmol) and *n*-butyllithium (Aldrich, 0.822 mL of a 2.5 M solution in hexane, 2.23 mmol) in dry THF at 0 °C. Stirring is continued at this temperature for 30 min. The reaction mixture is diluted with 15 mL of THF, quenched with 15 mL of saturated aqueous ammonium chloride, and extracted with methylene chloride. The organic layer is dried ($MgSO_4$), filtered, treated with ca. 2 g of silicagel, and concentrated *in vacuo* to a solid (product impregnated on silicagel), which is introduced at the top of a chromatography column packed with silicagel in hexane. Elution with hexane gives 0.286 g (66.2%) of ^{13}C-labeled diene: 97.4% of purity by GLC (column B); ^{1}H NMR (C_6D_6) 7.26–7.03 (m, 10 H), 6.33 (d, 1 H, J = 15.8 Hz), 6.16–6.07 (m, 1 H), 6.01–5.92 (m, 1 H), 5.15 (m, 1 H), 4.90–4.84 (m, 1 H), 2.59–2.48 (m, 2 H).

(*E*)-1,4-Diphenyl(1-^{12}C)hexa-1,5-diene. This compound is prepared by the method of Koch.[13a] A solution of *trans*-cinnamyl chloride (Aldrich; 11.1 g, 0.073 mol) in 25 mL of dry ether is added over a period of 40 min to a stirred mixture of Mg turnings (0.9 g) and iodine (~10 mg) in 5 mL of ether so as to maintain gentle reflux. After being boiled under reflux an additional hour, the reaction mixture is poured into an ice-cold, saturated, aqueous solution of ammonium chloride. The separated organic layer is washed with 5% ice-cold HCl and water, dried ($MgSO_4$), and concentrated *in vacuo*. GLC analysis of the residual pale-yellow oil on column A reveals a mixture of six compounds, retention times in min (% yield): A, 25 (30.6); B, 29 (0.4); C, 34 (52.2); D, 35 (0.3); E, 41 (6.3); and F, 49 (10.2). The crude product (6.5 g) is distilled under reduced pressure (1 mmHg), three fractions being collected in the temperature range 145–160 °C. Fraction 1 deposits crystalline *meso*-3,4-diphenylhexa-1,5-diene, which, after recrystallization from EtOH, has mp 85–85.5 °C (lit.[13a] mp 86–87 °C) and retention time 25 min (same as that for compound A; coinjection enhances this peak). Redistillation of fractions 2 and 3 gives compound C (retention time, 34 min): 4 g, 36%; ^{1}H NMR (C_6D_6) consistent with that of (*E*)-1,4-diphenylhexa-1,5-diene, 7.26–7.03 (m, 10 H), 6.33 (d, 1 H, J = 15.8 Hz), 6.16–6.07 (m, 1 H), 6.01–5.92 (m, 1 H), 5.04–4.99 (m, 1 H), 3.32 (q, 1 H, J = 6.45 Hz), 2.59–2.48 (m, 2 H). The residue from distillation, which crystallizes on cooling, is recrystallized from EtOH and affords 0.8 g (10.2%) of (*E*,*E*)-1,6-diphenylhexa-1,5-diene (compound G; retention time 49 min): mp 77.5–78 °C (lit.[13a] mp 78.8–79.2 °C); ^{1}H NMR (C_6D_6) 7.36–7.16 (m, 10 H), 6.44 (d, 2 H, J = 15.71 Hz), 6.30–6.24 (m, 2 H), 2.39 (t, 4 H, J = 3.32 Hz).

To obtain information on the structure of the remaining compounds formed in the reductive coupling of *trans*-cinnamyl chloride, the following experiments are performed.

Irradiation of (E,E)-1,6- and (*E*)-1,4-Diphenylhexa-1,5-diene (DPHD). A solution of (*E*,*E*)-1,6-DPHD (50 mg, 98.8% of purity, 1.2% 1,4-DPHD) and bibenzyl as sensitizer (3.5 mg) in benzene (3 mL) is irradiated with a sun lamp (375 W) under argon while being cooled with water. Aliquots are taken after 1, 2, and 6 h and analyzed by GLC on column A. The amount of (*E*)-1,4-DPHD stays constant within the run (1.1–1.2%). After 1 h, the reaction mixture contains 97.5% (*E*,*E*)-1,6-DPHD and 1.4% of compound E in a 97.5:1.4 ratio; after 2 h, the ratio is 95.8/3.1; and after 6 h, the mixture consists of 70.1% of (*E*,*E*)-1,6-DPHD, 26.2% of compound E, and 2.5% of compound D. Based on the order of their appearance during the irradiation, compounds D and E are tentatively assigned the structures (*Z*,*Z*)-1,6-DPHD and (*E*,*Z*)-1,6-DPHD, respectively.

Irradiation of (*E*)-1,4-DPHD (30 mg, purity 99.5%, containing 0.2% of compound B and 0.3% of (*E*,*Z*-)-1,6-DPHD) in 3 mL of benzene containing 3 mg of bibenzyl gives, after 2 h of irradiation, a mixture consisting of 19.9% of compound B, 75.7% of (*E*)-1,4-DPHD, and 0.6% of (*E*,*Z*)- and 0.3% of (*E*,*E*)-1,6-DPHD. Compound B accordingly is tentatively assigned the structure (*Z*)-1,4-DPHD.

Heating (E)-1,4-Diphenyl(^{12}C)hexa-1,5-diene at High Temperature. Aliquots of a 0.4% solution of (*E*)-1,4-DPHD in *o*-dichlorobenzene (20 mg in 5 mL) containing 11.1 mg of dihydroanthracene (15 molar equiv) are placed in several tubes. The tubes are degassed, sealed under vacuum, and heated in a Techne FB-07 fluidized alumina bath at 250 °C for 15, 30, and 60 min and at 300 °C for 15 min. Two additional experiments at 250 °C for 60 min are performed in benzene in the presence of 1.5 and 15 molar equiv of dihydroanthracene, respectively. GLC analysis on column B gives the results shown in Table 7.

Reaction of (*E*)-1,4-Diphenyl(^{12}C)hexa-1,5-diene in Thiophenol. A solution of 300 mg of (*E*)-1,4-DPHD (purity 93.3%, the remaining 6.7% consisting of the other isomers of DPHD as described above) in 15 mL of freshly distilled thiophenol (Aldrich) is placed in a Pyrex tube which is then degassed, sealed under vacuum and heated in the vapors of boiling anisole (154 °C) for 15.2 h (1 half-life, as determined in the kinetic study of the rearrangement, *vide infra*). The residue after removal of thiophenol by distillation is dissolved in ether (10 mL). The solution is washed with 5% NaOH and water, dried ($MgSO_4$), and concentrated *in vacuo* to a crude product (315 mg), which is flash chromatographed on silicagel. Elution with 2% ether–hexane gives a fraction (208 mg), GLC analysis of which on column A (oven temperature 210 °C, He 5 lb) shows it to consist of ten compounds [retention times in min (yield in %)]: 18 (18); 33 (33); 62 (33); 70 (6), and six minor compounds 20–60 (2–3). The

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[37] Doering, W. v. E.; Bragole, R. A. *Tetrahedron* **1966**, *22*, 385–391.

[38] Marvell, E. N.; Lin, C. *J. Am. Chem. Soc.* **1978**, *100*, 877–883.

[39] Newcomb, M.; Vieta, R. S. *J. Org. Chem.* **1980**, *45*, 4793–4795.

Table 8. The ^{1}H NMR Spectra of **1**(6-^{13}C) and **1**(3-^{13}C) Used for Analysis of Thermal Rearrangement

	benzene-d_6^{a}	toluene-d_8^{a}
1(6-^{13}C): 6-^{13}C; 3-^{12}C	4.75, 5.30; 2.50	4.73, 5.25; 2.48
1(3-^{13}C): 6-^{12}C; 3-^{13}C	5.05; 2.30, 2.75	5.00; 2.28, 2.70

^{a} In ppm from TMS.

Table 9. Effect of Pressure on Relative Areas in ^{1}H NMR Spectra of **1**(6-^{13}C) and **1**(3-^{13}C) after Heating **1**(6-^{13}C) for 60 000 s at 162 °C

	1(6-^{13}C)		**1**(3-^{13}C)		ratio	
p, bar	2H$_3$(^{12}C)	2H$_6$(^{13}C)	2H$_3$(^{13}C)	2H$_6$(^{12}C)	6-^{13}C:3-^{13}C	k_1^{a}
1^b	6.55	6.50	2.06	1.96	76.5:23.5	5.31
6000^b	2.82	2.80	2.01	2.07	57.9:42.1	15.33
1^c	6.39	6.29	1.99	1.99	76.1:23.9	5.41
6000^c	2.79	2.63	2.06	2.03	57.0:43.0	16.40

^{a} In units of 10^{-6} s^{-1}. ^{b} In benzene-d_6. ^{c} In toluene-d_8.

GC–mass spectrum of this fraction (column DB1, 15 m, oven temperature 100–250 °C, He 8 lb) shows that, with the exception of the first compound (m/z 153), all others have m/z 344, corresponding to addition products of thiophenol to DPHD: calcd for $C_{24}H_{24}S$, m/z 344. The complex NMR spectrum of this fraction shows a ratio of vinyl and methylene protons of 1:9, consistent with the majority of the addition compounds being derivatives of cyclopentane or cyclohexane.

Kinetics of the Thermal Rearrangement of (*E*)-1,4-Diphenyl(6-^{13}C)-hexa-1,5-diene {1(6-^{13}C)} to (*E*)-1,4-Diphenyl(3-^{13}C)hexa-1,5-diene {1-(3-^{13}C)}. (a) At Atmospheric Pressure. In preliminary experiments, 2 aliquots of a 2.4% solution of the diene (97.4% of purity) in C_6D_6, each in a tube of Pyrex and lead–potash glass, respectively, are degassed, sealed under vacuum, and heated at 154 °C (anisole vapor) for 27 h. The ratio of educt to product, as determined by integration of the NMR spectra (*vide infra*), is essentially the same for both specimens: 79.7/20.3 (Pyrex) and 80.4/19.6 (lead–potash). Since the nature of the glass makes essentially no difference, all subsequent experiments are performed in Pyrex.

Kinetic studies are effected in degassed deuteriobenzene (Cambridge Isotope Laboratory, 100%; 3 freeze–thaw cycles) in vacuum-sealed NMR tubes (No. 528 Pyrex) with 18-crown-6 ether as internal standard. Heating is in the vapors of appropriate liquids boiling under reflux. The tubes are withdrawn periodically for analysis and returned for further heating. Quantitative analysis of the almost degenerate rearrangement is effected by taking advantage of ^{13}C coupling with vinyl hydrogen atoms at C-6 and methylene hydrogen atoms at C-3 (**6-^{13}C**: 5.21–5.15 (m) and 4.90–4.84 (m); and 2.59–2.48 (m); and **3-^{13}C**: 5.05–4.99 (m); and 2.71–2.61 (m) and 2.45–2.35 (m)). Recovery is monitored by comparing the combined signals corresponding to the benzylic hydrogen atom at C-4 (3.32 (q), J = 6.45 Hz) and the singlet at 3.55 ppm in the standard. An acquisition time of 3.77 s and an interpulse delay time of 22 s is employed, 32–64 scans being accumulated for each measurement. Details of the calculation and corrections for compounds containing only ^{12}C and two ^{13}C are included as supplementary material in elaboration of the results in Table SI; results are shown in Table 2.

(b) Under High Pressure. Two solutions each of 25 mg of (*E*)-1,4-diphenyl(6-^{13}C)hexa-1,5-diene in 2 mL of benzene-d_6 and toluene-d_8, respectively, were prepared. Each was divided and introduced with sealing, one into polytetrafluoroethylene (PTFE) tubes that had been deactivated by prior treatment with triethylamine, the other into likewise deactivated glass ampules. The four samples were then heated for 60 000 s at 162 °C: the glass ampules at 1 bar, the PTFE tubes at 6000 bar. Quantitative analysis of **1**(6-^{13}C) and **1**(3-^{13}C) was effected by ^{1}H NMR using the signals shown in Table 8. The resulting ratios given in Table 9 are translated into the single-point first-order rate constants by means of the following equation: $2kt = \ln([\mathbf{1}]_0 - [\mathbf{1}]_{eq})/([\mathbf{1}] - [\mathbf{1}]_{eq})$ where $[\mathbf{1}]_0 = 100$, $[\mathbf{1}]_{eq} = 50$, and t = 60 000 s.

From the pressure dependence of the single-point first-order rate constants listed in Table 5, the activation volume was determined to be $\Delta V^{\neq} = -8.6 \pm 0.2$ cm^3 mol^{-1} (derived from the linear part of the slope in the pressure range between 530 and 2020 bar) and -9.5 ± 0.1 cm^3 mol^{-1} (derived from the nonlinear slope over the whole range of pressure [*vide infra*]).

(*E*)-1,1′-Bi-3-phenylcyclohex-2-enylidene. A solution of 1.0 g of 3-phenylcyclohex-2-enone[40] (mp 64–65 °C; lit.[40] mp 64.5–66 °C) in 10 mL of dry THF is added to a "titanium reagent", prepared from 5.5 g of $TiCl_4$, 3.04 g of activated zinc dust, and 0.48 mL of dry pyridine in 50 mL of dry THF, and processed in the usual manner.[35a] The crude product is extracted with CH_2Cl_2, dried (Na_2SO_4), and concentrated *in vacuo* to a yellow solid (0.76 g) consisting of (*E*)- and (*Z*)-1,1′-bi-3-phenylcyclohex-2-enylidene in the ratio 2/1, as determined by NMR. The solid is triturated in a mortar with 5 mL of THF to remove the much more soluble (*Z*) isomer. Filtration and washing with 2 mL of THF affords yellow crystals of (*E*)-1,1′-bi-3-phenylcyclohex-2-enylidene (BPC): 275 mg, 34%; >98% of purity; mp >203 °C dec; ^{1}H NMR (C_6D_6; assignments based on decoupling experiments) 7.42 (d, 4 H, J = 7.3 Hz (*o*,*m*), *o*-H), 7.17 (t, 4 H, J = 7.3 Hz (m,p), *m*-H), 7.10 (s, 2 H, J = 1.4 Hz, H-2), 7.07 (t, 2 H, J = 1.3 Hz (*p*,*o*), *p*-H), 2.44 (t, 4 H, J = 6.3 Hz, H-6), 2.36 (t, 4 H, J = 5.8 Hz, H-4), 1.62 (quintet, 4 H, J = 5.8 Hz, H-5); ^{13}C NMR ($CDCl_3$) 160.6, 160.0, 154.9, 154.2, 128.5, 128.0, 125.6. (*Z*)-1,1′-Bi-3-phenylcyclohex-2-enylidene: ^{1}H NMR (C_6D_6, assignments based on decoupling experiments) 7.50 (s, 2 H, J = 1.4 Hz, H-2), 7.38 (d, 4 H, J = 7.3 Hz (*o*,*m*), *o*-H), 7.10 (t, 4 H, J = 7.3 Hz (*m*,*p*), *m*-H), 7.02 (t, 2 H, J = 1.4 Hz (*p*,*o*), *p*-H), 2.36 (t, 4 H, J = 6.0 Hz, H-4), 2.28 (t, 4 H, J = 6.3 Hz, H-6), 1.68 (quintet, 4 H, J = 6.3 Hz, H-5); ^{13}C NMR ($CDCl_3$) 161, 155, 154, 151, 128, 124, 124.

Kinetics of the Interconversion of (*E*)- and (*Z*)-1,1′-Bi-3-phenylcyclohex-2-enylidenes 7 and 8. For the kinetic experiments, the NMR resonances of the methylene group in **7** and **8** at C–6 alone are suitable (2.28 and 2.44 ppm, respectively). The intervening resonances of the methylene groups at C–4 are both at 2.36 ppm and overlap very slightly but equally. A solution of ~3 mg of **7** in ~1 mL of C_6D_6 (Cambridge Isotope Laboratories; "100%" grade) is sealed under vacuum in a Pyrex NMR tube and heated in vapors of boiling liquids of appropriate boiling point. Rate constants are calculated by a nonlinear least-squares program that allows the starting concentration, x_0, the equilibrium concentration, x_e, and $(k_1 + k_{-1})$ to vary independently as a function of concentration, x, at time t. The primary data are given in Table SII as supplementary material. Specific rate constants and equilibrium constants and the derived Arrhenius and Eyring parameters are given in Table 6.

Pressure-Dependent Kinetics of the Thermal Rearrangement of *cis*-1,2-Divinylcyclobutane (*cis*-2) to 1,5-Cyclooctadiene (3) and the Rearrangement and Fragmentation of *trans*-1,2-Divinylcyclobutane (trans-2) to 3,4-Vinylcyclohexene (4) and 1,3-Butadiene (5). A mixture of *cis*-**2**, *trans*-**2**, and **4** was prepared photochemically from butadiene following the procedure of Hammond et al.[41] in the 15:78:7 ratio, respectively (lit.[41] 17:76:7). After separation by GC on a column packed with 20% silicone oil DC 550 on Chromosorb P (70 °C, He), ***trans*-2** and **4** were isolated each in >99% purity, while ***cis*-2** and **3**, the product of some rearrangement on the column, were obtained in a 90.2:9.8 ratio. Response factors were determined by GC analysis on column C of a solution consisting of ***trans*-2** (28.9 mg, 0.267 mmol; retention time (r.t.) 3.8 min), **3** (57.3 mg, 0.530 mmol; r.t. 10.1 min), **4** (45.6 mg, 0.422 mmol; r.t. 5.6 min), and *n*-nonane (38.7 mg, 0.302 mmol; r.t. 6.8 min) in *n*-heptane (370.6 mg, 3.70 mmol; r.t. 3.1 min). The following response factors were obtained: ***trans*-2**, 0.959 ± 0.003, **3**, 0.972 ± 0.015, and **4**, 0.988 ± 0.005 (***cis*-2** was assumed to be the same as ***trans*-2**).

Portions of a solution containing the mixture of ***cis*-2** and **3** obtained above (204.5 mg, 1.89 mmol) and *n*-nonane (198.3 mg, 1.55 mmol) in *n*-heptane (100 mL) were placed in the 7-kbar vessel and heated at 69.8 °C and the various pressures indicated in Table 3. At each pressure, the extent of rearrangement of ***cis*-2** to **3** was followed by GC to 70–80% of conversion. Recovery of ***cis*-2** and **3** as measured against the internal standard was >99%. Specific rate constants shown in Table 3 were calculated from the time dependence of the disappearance of ***cis*-2** according to the first-order rate law of irreversible reactions.

Portions of a solution containing ***trans*-2** (102.9 mg, 0.951 mmol) and *n*-nonane (128.5 mg, 1.00 mmol) in 100 mL of *n*-heptane were placed in a 7-kbar vessel and heated at 159.6 °C and the various pressures shown in Table 4. The reaction of ***trans*-2** to **3**, **4**, and **5** was followed by GC to 50–60% of conversion (at least six different times each). Since the analysis of butadiene **5** was not reproducible owing to its low boiling point, the amount of **5** was estimated as the difference between 100% and the recovery of ***trans*-2** to **3**, **4**, and **5** by GC against the internal standard. At each pressure the sum of the specific rate constants ($\sum k_1$) was

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Table 10. Temperature Dependence of Partial Molar Volumes (V, cm^3 mol^{-1}) in n-Heptane

T, °C	V(***trans*-2**)	V(***cis*-2**)[a]	V(**3**)[b,c]	V(**4**)[d]
20.0	140.0	135.4	122.6	130.4
25.0	140.9	136.4	123.1	131.1
30.0	142.2	136.8	123.7	131.8
35.0	142.7	137.6	124.1	132.5
40.0	143.4	138.4	124.5	133.2
45.0	143.9	139.1	124.9	133.6
50.0	144.7	139.9	125.3	134.3
55.0[a]	145.6		125.8	135.0
60.0[a]	146.5		126.3	135.8
65.0[a]	147.1		126.7	136.4
70.0[a]	148.3		127.3	137.1

[a] At temperatures higher than 50.0 °C, the rearrangement of ***cis*-2** → **3** takes place with measureable rate. [b] κ_{20}[e] = 3.894 ± 0.007 (***cis*-2** → **3**). [c] κ_{20}[e] = 3.829 ± 0.028 (***trans*-2** → **3**). [d] κ_{20}[e] = 2.526 ± 0.039 (***trans*-2** → **4**). [e] κ_{20} in units of 10^{-3} K^{-1}.

determined from the time dependence of the disappearance of ***trans*-2**. The individual specific rate constants in Table 4 were obtained by a Marquardt optimization routine.[42]

The volume of activation ($\Delta V^{\neq}$) was calculated from the linear part of the slope of the correlation of ln k_1 against p ($\ln k_1 = a_1 + b_1 p$; $\Delta V^{\neq} = b_1 RT$).[43] The linearity holds up to p = 1 kbar for the reaction of ***cis*-2** to **3** (Table 3) and 3 kbar for the reaction of ***trans*-2** to **3**, **4**, and **5** (Table 4) (for results, see Scheme 2). For the reaction of ***cis*-2** to **3**, $\Delta V^{\neq}$ was also derived by a quadratic equation ($\ln k_1 = a_2 + b_2 p + c_2 p^2$; $\Delta V^{\neq} = -b_2 RT$), which is valid over the entire range of pressures and gives rise to the value $\Delta V^{\neq} = -13.4 \pm 0.6$ cm^3 mol^{-1}, in agreement within experimental uncertainty with the value from the simpler treatment.

Reaction Volumes. Partial molar volumes (V) of ***trans*-2**, **3**, and **4** were determined from the density (d) of solutions measured for various concentrations (c) and temperatures listed in Table 10 by using the following equation: $\Phi = (M/d_0)[(1000/c) \times (d - d_0)/d_0]$ (M, molecular weight; d_0, density of pure solvent),[44] a linear extrapolation of Φ to c = 0. V(***cis*-2**) was determined from the density of a solution containing a mixture of 90.2% ***cis*-2** and 9.8% **3**. The reaction volumes shown in Scheme 2 are calculated from the partial molar volumes in Table 10: $\Delta V^{R} = V$(product) − V(educt). From the temperature dependence of the reaction volumes, the temperature coefficients κ_{20} can be calculated with the equation given by El'yanov et al.,[45] $\Delta V^{R}(T) = \Delta V^{R}(T_0)[1 + \kappa_{20}(T - T_0)$; T_0 = 20 °C. The κ_{20} values listed in Table 10 are of the same order of magnitude as the general value ($\kappa_{20} = 4.4 \times 10^{-3}$ K^{-1}) reported by El'yanov et al.[45]

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Supplementary Material Available: Table SI and Table SII contain the unprocessed experimental data from which Tables II and VI are derived, respectively. Details of the calculations of the kinetics of the rearrangement of **1(6-^{13}C)** (Scheme 1) are also given (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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