

(8) The 3-21G basis set (and perhaps all split-valence shell basis sets) appears to be less satisfactory than the minimal STO-3G basis set for analyzing TB interactions involving virtual π^* orbitals. This may be due to the fact that the spacings between the π^* and σ^* manifolds are actually more realistic in the minimal basis set. Of course, if proper calculations of the anion states were carried out, for example by using the stabilization method, then the more flexible basis sets would be expected to yield more reliable results.⁵⁸

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A "Frustrated" Cope Rearrangement: Thermal Interconversion of 2,6-Diphenylhepta-1,6-diene and 1,5-Diphenylbicyclo[3.2.0]heptane

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Abstract: The title reaction constitutes a reliable model of a nonconcerted, diradical mechanism closely related to a Cope rearrangement. Its activation parameters relate to a transition state approximated by 1,5-diphenylcyclohepta-1,5-diyl (7). Force field calculations of various conformations of the diradical model the reaction path and reproduce the "experimental" enthalpy of formation of the rate-determining transition state. The experimental enthalpy of activation of the "degenerate" Cope rearrangement of 2,5-diphenylhexa-1,5-diene-1,6-¹³C₂ (2) is essentially identical with an enthalpy of activation calculated by force field for the model 1,4-diphenylcyclohexa-1,4-diyl (6). Strong support is thereby provided for this Cope rearrangement proceeding by a mechanism of the "continuous diradical" or "diradical-as-transition-state" type.

Diradical-Intermediated Cope Rearrangement. Skeptical of the widespread conviction that the Cope rearrangement¹ should be concerted in mechanism in all cases without exception, the suggestion was made in 1971² that energetics, biased more or less deliberately by employing the enthalpy of formation of the isopropyl radical being advocated at the time by Tsang,^{3a} admitted the intermediacy of diradical cyclohexa-1,4-diyl (1) as a mechanistic alternative worthy of serious consideration. Later, when a seemingly more accurate but higher value for isopropyl radical pointed to a difference of -6.8 kcal/mol between the experimental enthalpy of formation of the transition state and the estimated enthalpy of formation of the hypothetical diradical (enthalpy of concert, $\Delta H_{ct} = \Delta_f H^\ddagger - \Delta_f H^\circ(1)$),^{4b} the archetypal Cope rearrangement of hexa-1,5-diene was restored securely to the land of concert. (The energy of concert becomes -11.0 kcal/mol if a more recent value from Tsang^{3c} for isopropyl radical is accepted.)⁵

Wehrli, Schmid, Belluš, and Hansen⁶ and Dewar and Wade⁷ responded to the 1971 provocation by exploring the inference that radical-stabilizing substituents such as cyano⁶ or phenyl^{7a,b,c} in the 2- and 5-positions could move the mechanism into the domain of diradical-as-intermediate. The two groups found marked acceleration of rearrangement in 2,5-dicyano- and 2,5-diphenylhexa-1,5-diene (2), respectively, and concluded that the diradical mechanism (6 in Scheme I) was operating. A subsequent, more thorough, thermochemical analysis of the rearrangement of 2^{4a} lent further support to the conclusion. That analysis had depended on the reliabilities of the heats of formation of styrene and α -methylstyrene⁸ (used for estimation of the enthalpy of conjugation between a phenyl group and a double bond) and the heat of formation of benzyl radical as recently evaluated by Rossi and Golden.⁹

Our response to the 1971 suggestion attempts to develop a credible diradical model to compare with the Cope rearrangement. Such a model is a "frustrated" Cope rearrangement, created by

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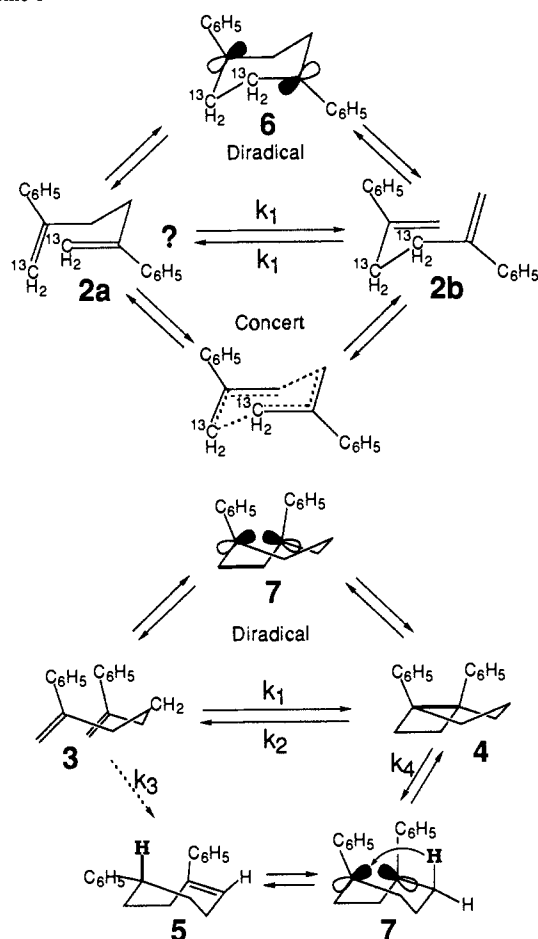
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[†] Ruhr-Universität.

[‡] Harvard University.

Scheme I



insertion of a seventh carbon atom (CH_2) between C-3 and C-4 of hexa-1,5-diene (Scheme I). The resulting system would still be able to engage in the first phase of the Cope rearrangement (formation of a single bond between the ends of the double bonds) but would be quite unable to complete the second phase (fragmentation of the C-3,C-4 single bond). The device would frustrate the Cope no matter if it were concerted or diradical in mechanism. This approach involves little more than recognition of the identity of the first step in the hypothetical diradical-Cope and the first, diradical-generating step in the cycloaddition reaction of olefins.¹⁰ The concept is realized in 2,6-diphenylhepta-1,6-diene (3) as an authentic diradical model for the Cope rearrangement of 2,5-diphenylhexa-1,5-diene (2). It was assumed artlessly that thermochemical measurements, simple estimations, and force field calculations would be able to deal convincingly with the various complications introduced by the seven-membered ring.

"Frustrated" Cope: 2,6-Diphenylhepta-1,6-diene (3). Initial studies¹¹ demonstrated the feasibility of the approach. When 3 was heated in the range 176–225 °C, it (pseudo)equilibrated with the product of intramolecular cycloaddition, 1,5-diphenylbicyclo[3.2.0]heptane (4) (Scheme II). Subsequently, a practically irreversible, intramolecular ene reaction to 1,5-diphenylcycloheptene (5) was discovered and incorporated into the kinetic scheme. In early quantitative studies, kinetics were rendered unacceptably inaccurate by the formation of byproducts, albeit in small amount. These difficulties have now been largely overcome.

The structure of 4 was assigned on the basis of two methods of preparation as shown in Scheme II. First, irradiation of 1,4-diphenylcyclohepta-1,3-diene according to Courtot,¹³ followed by

Scheme II

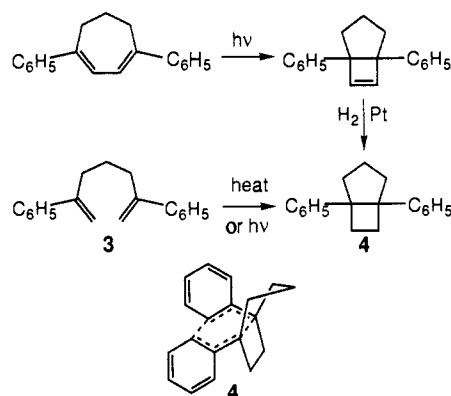


Table I. Specific Rate Constants for the Systems 3, 4, and 5 Calculated on the Basis of Three Models: Four Rate Constants of Scheme I Active (Model 4), k_4 Inactive (Model 3: $k_4 = 0$), and k_3 Inactive (Model 3: $k_3 = 0$)

T, °C	$10^6 k_1, \text{s}^{-1}$	$10^6 k_2, \text{s}^{-1}$	$10^6 k_3, \text{s}^{-1}$	$10^6 k_4, \text{s}^{-1}$
Model 4				
194.4	1.99 ± 0.03^a	1.45 ± 0.03	0.04 ± 0.02	0.09 ± 0.02
207.3	4.69 ± 0.06	4.68 ± 0.06	0.11 ± 0.05	0.30 ± 0.05
220.3	10.39 ± 0.09	14.21 ± 0.10	0.23 ± 0.08	0.97 ± 0.08
234.8	25.5 ± 0.6	46.6 ± 0.6	0.66 ± 0.49	3.35 ± 0.49
243.3	41.7 ± 0.8	89.7 ± 0.8	1.14 ± 0.62	6.69 ± 0.69
mean ^b	$\pm 1.52\%$	$\pm 1.19\%$	$\pm 51.5\%$	$\pm 15.0\%$
Model 3: $k_4 = 0$				
194.4	1.98 ± 0.05^a	1.49 ± 0.04	0.06 ± 0.04	
207.3	4.66 ± 0.15	4.83 ± 0.14	0.17 ± 0.12	
220.3	10.3 ± 0.3	14.7 ± 0.3	0.45 ± 0.23	
234.8	25.1 ± 0.9	48.1 ± 0.9	1.4 ± 0.7	
243.3	40.9 ± 2.7	92.7 ± 2.7	2.6 ± 2.1	
mean ^b	$\pm 3.74\%$	$\pm 2.49\%$	$\pm 64.2\%$	
Model 3: $k_3 = 0$				
194.4	2.01 ± 0.03^a	1.44 ± 0.03		0.10 ± 0.03
207.3	4.75 ± 0.07	4.67 ± 0.08		0.32 ± 0.06
220.3	10.5 ± 0.1	14.2 ± 0.1		1.0 ± 0.1
234.8	25.9 ± 0.4	46.5 ± 0.4		3.5 ± 0.3
243.3	42.4 ± 0.8	89.6 ± 1.0		7.0 ± 0.8
mean ^b	$\pm 1.44\%$	$\pm 1.33\%$		$\pm 15.2\%$

^aDeviations reported at the 95% confidence level. ^bMeans of the uncertainties converted to percent.

catalytic hydrogenation of the resulting 1,5-diphenylbicyclo[3.2.0]hept-6-ene, led to 4. Second, irradiation in benzene solution of 2,6-diphenylhepta-1,6-diene (3), prepared from glutaric acid according to the procedure of Marvel and Gall,¹² also produced 4. These samples are identical with a sample from the thermal rearrangement of 3.

When heating of 3 is much prolonged (401 h, 220.3 °C, *o*-dichlorobenzene), a new substance, 1,5-diphenylcycloheptene (5), can be isolated from a mixture consisting of 3 (32.2%), 4 (18.9%), 5 (48.9%), and unidentified byproducts (3.8%) (Scheme I). The structure of 5 is fully consistent with ¹H and ¹³C NMR spectra and the results of complete, circumannular, decoupling experiments (see Experimental Section for details).

The kinetics of the reaction are elucidated in the temperature range 194.4–243.3 °C, in *o*-dichlorobenzene, a solvent determined, after several exploratory experiments, to lead to fewer byproducts. The resulting data (see Table VI) can be fit to three models, each of which includes the interconversion of 3 and 4 (k_1 and k_2): Model 4, in which 5 is formed from both 3 and 4 (k_3 and k_4 active; see Scheme I); Model 3, $k_4 = 0$, in which 5 is formed from 3 alone ($k_4 = 0$; k_3 active); and Model 3, $k_3 = 0$, in which 5 is not formed directly from 3, but only indirectly from 4 ($k_3 = 0$; k_4 active).

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Table II. Arrhenius Parameters for Thermal Isomerization of the System 2,6-Diphenylhepta-1,6-diene (3), 1,5-Diphenylbicyclo[3.2.0]heptane (4), and 1,5-Diphenylcycloheptene (5)

k_i^a	E_a^b	$\log A$	ΔH^{*b}	ΔS^{*c}
Model 4 ^d				
k_1	29.84 ± 0.63	8.24 ± 0.27	28.86 ± 0.63	-23.80 ± 0.99
k_2	40.49 ± 0.15	13.09 ± 0.06	39.51 ± 0.15	-1.64 ± 0.28
k_3	32.56 ± 2.65	7.83 ± 1.11	31.59 ± 2.65	-25.72 ± 2.78
k_4	42.33 ± 0.34	12.74 ± 0.14	41.35 ± 0.34	-3.24 ± 0.56
Model 3: $k_3 = 0$				
k_1	29.90 ± 0.59	8.28 ± 0.30	28.93 ± 0.59	-23.65 ± 1.07
k_2	40.54 ± 0.14	13.11 ± 0.06	39.56 ± 0.14	-1.55 ± 0.26
k_4	41.77 ± 1.07	12.51 ± 0.36	40.79 ± 1.37	-4.27 ± 1.49

^a Isomerizations of 3 to 4 (k_1), 4 to 3 (k_2), 3 to 5 (k_3), and 4 to 5 (k_4), respectively (see Scheme I). ^b In kcal/mol. ^c Entropy units. ^d Deviations reported at the 95% confidence level.

The resulting specific rate constants are obtained by a Marquardt optimization routine¹⁴ and are given in Table I along with their attendant uncertainties.

In the two models having k_3 active, uncertainties in the calculated values of k_3 are strikingly large (Model 4 and Model 3, $k_4 = 0$). Use of the latter model also leads to significantly larger uncertainties in the values of k_1 and k_2 , by factors of 2.5 and 2.1, respectively. Complete exclusion of k_3 as a significant process in the overall scheme does not lead to enhanced uncertainty in k_1 , k_2 , or k_4 . In the interests of economy, we feel justified in staying with Model 3 ($k_3 = 0$) until such time as more accurate data relating to the formation of 5 dictate otherwise. We do not thereby imply that k_3 is strictly equal to zero, only that it is substantially smaller than k_4 .

Activation parameters and enthalpies and entropies of activation associated with Model 4 and Model 3 with $k_3 = 0$ are collected in Table II.

A necessary but insufficient condition for a concerted, intramolecular ene mechanism for the direct conversion of 3 to 5 requires $k_4 = 0$. Such a mechanism will not be considered further, though the temptation to rationalize its failure to dominate is hard to resist. A diradical-mediated mechanism requiring a "boat-like", "endo" conformation that is generated only from 4 and to little or no extent from the initially "exo" set of conformations stemming directly from 3 is consistent with Model 3 ($k_3 = 0$) (vide infra Figure 1).

"Degenerate" Cope: 2,5-Diphenylhexa-1,5-diene (2). The "degenerate" Cope rearrangement of 2,5-diphenyl-3,3,4,4-tetra-deuteriohexa-1,5-diene has already been reported.^{7a-c} "However, there are in fact good reasons for regarding the published experimental values with suspicion. The activation parameters for 2(1)^{7b} were derived from just two measurements¹⁵ at two temperatures...."^{7b} Prudence called for a repetition.

In that effort, deuterium has been replaced by ¹³C in order to avoid complicating secondary isotope effects. The preparation of 2,5-diphenylhexa-1,5-diene-1,6-¹³C₂ (2a) from 1,2-dibenzoyl-ethane follows the procedure of Greenwald, Chaykovsky, and Corey¹⁶ but uses ¹³C-methyltriphenylphosphonium iodide (99.42% ¹³C). The reversible thermal rearrangement of 2a to 2b in hexadeuteriobenzene is a clean reaction that can be followed quantitatively by ¹H NMR. For details, see the Experimental Section, where the data, corrected for normal abundance of ¹³C, are given in Table VII.

Specific rate and equilibrium constants are calculated by nonlinear, least-squares regression and are shown in Table III,

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(15) In his defense, Wade's comment (p 99)^{7c} should be heard: "No claim as to the accuracy of these values is made since only two rate measurements were used to calculate them." Original data not being reported in papers or dissertation, the conclusions ($k_1 = 6.1 \pm 0.1$ at 82.25 °C; $k_1 = 28.5 \pm 0.8$ at 100.95 °C) cannot be verified, but, from the plots in Figures 42 and 43, "The standard deviations for these rates was (sic) reasonably good."

(16) Greenwald, R.; Chaykovsky M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128-1129.

Table III. Rate and Equilibrium Constants and Arrhenius Parameters for the Reversible Rearrangement of 2,5-Diphenylhexa-1,5-diene-1,6-¹³C₂ (2a) and 2,5-Diphenylhexa-1,5-diene-3,4-¹³C₂ (2b) in Benzene-*d*₆

T , °C	k_1 , 10 ⁻⁵ s ⁻¹	K^a
58.40 ± 0.08 ^b	0.184 ± 0.002 ^b	1.004
70.08 ± 0.04	0.577 ± 0.006	0.999
81.25 ± 0.03	1.61 ± 0.02	1.005
94.06 ± 0.04	4.83 ± 0.11	1.003
107.83 ± 0.05	14.10 ± 0.14	0.996
$E_a = 21.98 \pm 0.18^b$ kcal/mol		
$\Delta H^* = 21.28 \pm 0.18$ kcal/mol (83.1 °C)		
$\log A = 8.76 \pm 0.15$		
$\Delta S^* = -20.75 \pm 0.45$ eu (83.1 °C)		

^a Calculated by an optimization procedure in which K is allowed to vary. ^b Uncertainties are reported at the 95% confidence level.

as are derived Arrhenius parameters and enthalpy and entropy of activation. The values obtained by Dewar and Wade^{7b} from "two measurements" at 82.25 and 100.98 °C ($E_a = 21.91$ kcal/mol; $\log A = 8.86$) are in spectacular agreement—"wondrous strange".¹⁷

Thermochemistry: Dienes 2 and 3. In order to relate the diradical hypothesized in the interconversion of 3 and 4 to the Cope rearrangement of 2, an enthalpy profile is needed. Although $\Delta_f H^\circ$ [styrene] = +35.4 ± 0.4 kcal/mol is known and that of α -methylstyrene is available for the liquid ($\Delta_f H^\circ(l) = +16.85$ kcal/mol),⁸ it seems important to obtain trustworthy heats of formation for 2 and 3. This has now been done by determining heats of hydrogenation directly by the method of Roth and Lennartz.¹⁸ Corrections for differences in heats of solvation between diene and saturated hydrocarbon are assumed to be -0.2 kcal/mol while differences in heats of vaporization are based on Kováts indices. Greater detail is to be found in a related discussion by Roth et al.¹⁹ Experimental results are given in Table IV. Comparison of the values of $\Delta H^\circ(H_2)$ of 2 and 3 with those of hexa-1,5-diene ($\Delta H^\circ(H_2) = -60.1$ kcal/mol) and hepta-1,6-diene ($\Delta H^\circ(H_2) = -60.2$ kcal/mol), respectively, reveals a change in heat of hydrogenation when CH₂=CHR is replaced by CH₂=C(C₆H₅)R of +2.0 kcal/mol. The corresponding value for replacement of H by alkyl, CH₂=CHR by CH₂=CR'R, is +1.9 kcal/mol. It is interesting in passing to recall that $\Delta \Delta H^\circ(H_2)$ for the replacement of H by vinyl is 6.6 kcal/mol (ethene-butadiene: propene-*trans*-piperylene) and 5.1 kcal/mol (propene-isoprene).

In order to translate the heats of hydrogenation into heats of formation, heats of formation of the corresponding products of hydrogenation need to be estimated. Application of force field calculation²⁰ allows differences between meso and racemic configurations (and any unsuspected nonbonded interactions) to be incorporated. The estimated $\Delta_f H^\circ$ are +11.25 for the mixture of 2,5-diphenylhexanes resulting from hydrogenation (54.4% meso, +11.20; 45.6% rac, +11.32) and +5.96 kcal/mol for 2,6-diphenylheptane (the mean of meso, +5.77, and racemic, +6.15). Another approach, involving application of twice the value,

(17) Humbled, WvED apologizes to Dewar and Wade for ever having had doubts, but not without admitting to speculations that the sage of Austin is on-line to the Delphic oracle; possesses the ultimate computational program, which a secretive US Air Force has requested not be revealed; and is a deserved beneficiary of Pasteur's Postulate. "Chance favors the prepared mind."

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(19) Roth, W. R.; Lennartz, H.-W.; Doering, W. von E.; Dolbier, W. R.; Schmidhauser, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 1883-1889.

(20) Force field calculations were performed by the MM2 program of Allinger,²¹ augmented and improved by W. R. Roth and F. Bauer (*Chem. Ber.* MM2(aug); in preparation) in five ways: (a) conjugated systems of olefins are handled without resort to SCF calculation; (b) radicals of the benzyl type are treated by setting their stabilization energy equal to that of allyl; (c) heats of formation of simple primary, secondary, and tertiary radicals as recommended by Gutman et al.⁵ are incorporated; (d) the cyclobutane ring is reparametrized by employing all relevant thermochemical data currently available; (e) an error in the commercially available MMP2 program is corrected.

Table IV. Heat of Hydrogenation of 2,5-Diphenylhexa-1,5-diene (2) and 2,6-Diphenylhepta-1,6-diene (3)

substrate ^a	titration, mol/s × 10 ⁷	catalyst, g	H ₂ uptake, mol/s × 10 ⁶	energy, mcal/s	-ΔH(H ₂), kcal/mol	-ΔH(H ₂), ^b kcal/mol
2	0.6752	0.03899	0.1371	3.8098	55.58	56.65 ± 0.2
2	0.6752	0.04188	0.1357	3.7976	55.97	
3	0.7326	0.04333	0.1455	4.0013	55.00	55.67 ± 0.2
3	0.7326	0.04333	0.1469	4.0288	54.84	
3	0.7289	0.04247	0.1449	3.9746	54.86	
3	0.7289	0.04247	0.1455	3.9700	54.56	

^a In solution in isooctane. ^b Corrected for differences in heats of solution and vaporization of educt and product (see text).

$\Delta\Delta_f H^\circ [\text{CHH}/\text{CH}(\text{C}_6\text{H}_5)] = +25.70$,²² to $\Delta_f H^\circ [n\text{-hexane}] = -39.94$ kcal/mol and to $\Delta_f H^\circ [n\text{-heptane}] = -44.86$ kcal/mol,⁸ leads to $\Delta_f H^\circ [2,5\text{-diphenylhexane}] = +11.46$ and $\Delta_f H^\circ [2,6\text{-diphenylheptane}] = +6.54$ kcal/mol. Mean values for heats of formation of 2 and 3 are +68.0 and +61.9 kcal/mol, respectively.²³

1,5-Diphenylbicyclo[3.2.0]heptane (4). An "experimental" heat of formation of 4 is obtained by subtracting the difference, $\Delta\Delta H^\ddagger = +10.6$ kcal/mol, between the enthalpies of activation for the conversions of 3 to 4 (+28.9₃ kcal/mol) and of 4 to 3 (+39.5₆ kcal/mol) (see Table II, Model 3, $k_3 = 0$) from the heat of formation of 3: there results $\Delta_f H^\circ [4] = +51.3$ kcal/mol.

An estimated value of +54.0 kcal/mol results from twice adding the difference (+26.67 kcal/mol) between $\Delta_f H^\circ$ of *tert*-butylbenzene (-5.40 kcal/mol) and that of isobutane (-32.07 kcal/mol), the only relevant pair in the literature,⁸ to $\Delta_f H^\circ$ [bicyclo[3.2.0]heptane] = +0.7 kcal/mol as calculated by MM2(aug).²⁰ (By way of calibration, MM2(aug) gives values of 67.5 and 62.0 kcal/mol respectively for $\Delta_f H^\circ$ of 2 and 3.) Calculation entirely by MM2(aug) gives values of +54.5 and +57.3 kcal/mol, respectively, for *endo*- and *exo*-1,5-diphenylbicyclo[3.2.0]heptane. These calculated values for 4 being significantly higher than the "experimental" value seems the more surprising because any contribution from steric interaction between the two phenyl groups would have been thought to be energy-raising, not energy-lowering.

Compound 4 appeared a likely candidate for operation of a proposal, recently advanced by Pettersson and Liljefors,²⁴ that a term for electrostatic interaction is required to calculate correctly conformations of compounds having proximate pairs of benzene rings. Application of their program results in a predicted heat of formation for 4 of 56.1 kcal/mol. Until our hope to establish the relationship of the two phenyl groups by an X-ray crystallographic determination of structure is realized, we can only speculate that the energy lowering may originate in a long 1.5 bond and concomitant chair-like overlap of the two, then incipiently benzyl-like phenyl rings (Scheme II).

1,5-Diphenylcycloheptene (5). Estimation of $\Delta_f H^\circ$ [1,5-diphenylcycloheptene] stems from $\Delta_f H^\circ$ [cycloheptene] = -2.20,⁸ by addition of +25.7²² and +23.6 kcal/mol.²³ $\Delta_f H^\circ [5] = +47.1$ kcal/mol. Because this model contains the same amount of strain as cycloheptene, the value calculated by MM2(aug) for the chair conformation is preferable: $\Delta_f H^\circ [5] = +46.2$ kcal/mol.

Discussion

It is the presupposition of this work that inter- and intramolecular, thermal dimerizations of olefins and cycloreversions of their conjugate cyclobutanes involve a diradical and proceed by a non-concerted mechanism. The paradigm is the "forbidden" dimerization of ethylene to cyclobutane, for which an enthalpy of activation of 43.5 kcal/mol ($\Delta_f H^\ddagger = 68.6$ kcal/mol) is estab-

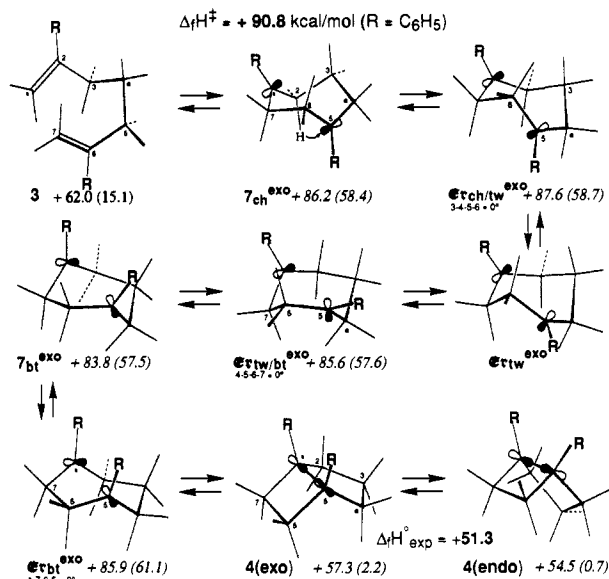


Figure 1. Various conformations of the diradical 7 (R = C₆H₅) and the parent diradical (R = H) on the way from 2,6-diphenylhepta-1,6-diene (3) to 1,5-diphenylbicyclo[3.2.0]heptane (4) and, hypothetically, hepta-1,6-diene to bicyclo[3.2.0]heptane, respectively, along with their enthalpies of formation as calculated by MM2(aug). Conformations designated 7 are local minima: those designated "Er" (En route) are selected as reasonable steps on the way. Some are unequivocally defined by fixing the noted dihedral angle equal to 0°. Values are enthalpies of formation in kcal/mol for R = C₆H₅, shown first, and, following in parentheses, values for R = H.

lished.^{4a} Support for the procedure that employs an estimated enthalpy of formation of the hypothetical diradical-as-intermediate to model the experimental enthalpy of activation is adduced by analysis of the paradigm. Thus, $\Delta_f H^\circ$ [tetramethylene] is estimated to be +67.4 kcal/mol by taking $\Delta_f H^\circ$ [butane] = -30.4 kcal/mol and $\Delta\Delta_f H^\circ [\text{CH}_3\text{CH}_2\text{H}/\text{CH}_3\text{CH}_2^\cdot] = +48.9$ kcal/mol according to Gutman et al.^{3a} Agreement between experimental transition state and estimated heat of formation of tetramethylene diradical is good.

The intermolecular example closest to the intramolecular example of this work is the dimerization of styrene²⁵ to 1,2-diphenylcyclobutane and its cycloreversion.²⁶ However, when the activation parameters of those papers are converted to heats of formation of their respective transition states by use of the known $\Delta_f H^\circ$ of styrene and estimation of $\Delta_f H^\circ$ of diphenylcyclobutane, these values, which should have been identical, differ from each other by ~10 kcal/mol. Only a careful experimental reexamination can hope to improve the reliability to a point where the example can serve as a check on the accuracy of MM2(aug) as it is applied to diphenyl diradicals.

In order to make effective use of the presupposition of this work, that the interconversion of 3 and 4 not be a concerted process, but involve a noninteractive diradical of the 1,5-diphenylcyclo-

(21) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127-8132.

(22) The change in heat of formation accompanying replacement of CH₂ by CH(C₆H₅) is estimated from the three pairs of $\Delta_f H^\circ$:⁸ propane, -25.0; isopropylbenzene, +1.0; butane, -30.36; 2-phenylbutane, -4.76; cyclohexane, -29.49; phenylcyclohexane, -4.0. There results a mean value for $\Delta_f H^\circ$ (CHH/CH(C₆H₅)) = +25.70 ± 0.27 kcal/mol.

(23) The corresponding value for replacement of vinyl hydrogen by phenyl, $\Delta\Delta_f H^\circ [\text{CH}_2=\text{CRH}/\text{CH}_2=\text{CR}(\text{C}_6\text{H}_5)]$, is 23.6 ± 0.3 kcal/mol.

(24) Pettersson, I.; Liljefors, T. *J. Comput. Chem.* **1987**, *8*, 1139-1145.

(25) Shurava, V. N.; Katsobashvili, V. Ya. *React. Kinet. Catal. Lett.* **1977**, *7*, 267-272.

(26) Jones, G., II; Chow, V. L. *J. Org. Chem.* **1974**, *39*, 1447-1448.

hepta-1,5-diyl 7 family (see Figure 1, R = H) as intermediate or transition state, the experimental heat of formation of the transition state must be mimicked by force field calculation before that program can be confidently used to estimate the heat of formation of the hypothetical 1,4-diphenylcyclohexa-1,4-diyl 6.

As a test of how well MM2(aug)²⁰ handles the steric problems in the seven-membered ring, the thermal rearrangement of bicyclo[3.2.0]heptane to hepta-1,6-diene may serve.^{27b,c} However, the reaction is not clean, hepta-1,6-diene being one of several products and itself decomposing to butadiene and propene. A further defect in this example is the failure of the reverse reaction, the thermal rearrangement of hepta-1,6-diene, to give detectable amounts of bicyclo[3.2.0]heptane, butadiene and propene being the only reported products.^{27a} Nonetheless, the value for $\Delta_f H^\circ$ [bicyclo[3.2.0]heptane] = +0.68 kcal/mol, calculated by MM2(aug), and the experimental enthalpy of activation, ΔH^\ddagger = +61.8 kcal/mol, translate into $\Delta_f H^\ddagger$ = +62.5 kcal/mol. Among the various conformations identified in Figure 1 as local minima or fixed as possible transition states, the highest enthalpy of formation, $\Delta_f H^\circ$ = +61.1 kcal/mol, is calculated by MM2(aug) for Er_{bt}^{exo} (R = H), a quite reasonable, immediate product of ring opening en route to the product of cleavage, 3 (R = H). Agreement is good, particularly so, in mind of the inability of MM2(aug) to deal with the relative rates of decline in ring strain and in bonding energy between the incipient radical centers as the ring opens: that is, MM2(aug) is in no way designed to locate the rate-determining transition state. This procedure is therefore expected to err on the low side, no allowance being possible for situations in which growth of strain is not fully paid for by growth of bonding.

2,6-Diphenylhepta-1,6-diene (3). The "forbidden" cyclization of 3 is initiated by bonding between C-1 and C-7 in a conformation (antiperiplanar were best) that minimizes energy-raising overlap (the "verbot") between the radicals emerging at C-1 and C-4. The immediate result is diradical 7 in the chair conformation of the exo family (7_{ch}^{exo} of Figure 1, R = C₆H₅).²⁸ Concerted cyclization to 4 from this conformation is thwarted by its intrinsically "forbidden" nature and by the prohibitive strain in the expected *trans*-4. The hypothetical diradical is thus formulated as an intermediary diradical that is transformed by an elaborate sequence of internal-rotational processes into a suitable conformation. It is hypothesized to pass through a "twist" conformation (Er_{tw}^{exo} of Figure 1, R = C₆H₅) on its way to a "boat" conformation, 7_{bt}^{exo} , befitting cyclization to *cis*-4. At some point during this sequence, overlap of orbitals C-1 and C-4 is nullified and closure to 4 becomes "neutral" in the Woodward-Hoffmann sense,³⁰ neither "forbidden" nor "allowed".

In the absence of a complete multidimensional, topographical mapping of the surface by the type of quantum mechanical treatment that lies some distance in the future, MM2(aug)^{20,31}

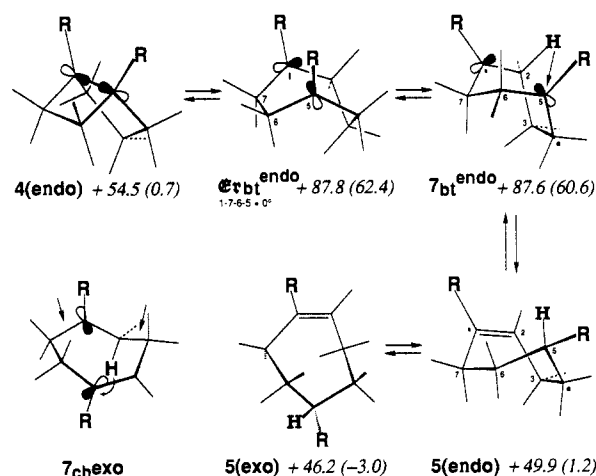


Figure 2. Various conformations of the diradical 7 (R = C₆H₅) and the parent diradical (R = H) on the way from 1,5-diphenylbicyclo[3.2.0]heptane (4) to 1,5-diphenylcycloheptene (5) and, hypothetically, bicyclo[3.2.0]heptane to cycloheptene, respectively, along with their enthalpies of formation in kcal/mol as calculated by MM2(aug). Conformations 7_{bt}^{endo} are local minima; Er_{bt}^{endo} (En route) are selected as reasonable steps on the way and are unequivocally defined by fixing the noted dihedral angle equal to 0°. Values are enthalpies of formation in kcal/mol for R = C₆H₅, shown first, and, following in parentheses, values for R = H.

is used to locate two local minima (in what we hope is not too egregious neglect of orbital overlap) and other points en route, well defined by setting a specified dihedral angle at 0°. The highest point located in that far-from-exhaustive way is $Er_{ch/tw}^{exo}$, $\Delta_f H^\circ$ = 87.6 kcal/mol. This point probably represents a minimum value for the barrier determining the rate of moving from conformation 7_{ch}^{exo} to that terrain from which collapse to 4^{exo} occurs with no further hurdle. A higher point may lie along the paths of conformational change or be found as a true transition state close in conformation to that of the product.

The discrepancy between calculated $Er_{ch/tw}^{exo}$ at +87.6 kcal/mol and the experimental transition state at +90.8 kcal/mol is very likely maximal and represents our best shot. There is no room for entertaining an enthalpy of concert: the presupposition of no concert in the interconversion of 3 and 4 is securely confirmed.³⁵

In terms of the strategy of this work, the data from the interconversion of 3 and 4 are being used indirectly to evaluate the ability of MM2(aug) to handle the energetics including the elements of strain in the seven-membered ring and in the interaction of the ortho hydrogen atoms of the benzene rings with proximate hydrogen atoms of the seven-membered ring. If agreement with experiment is less than perfect, it misses on the low side by an amount (3.2 kcal/mol) that is not hard to rationalize. We therefore have considerable confidence in the application of MM2(aug) to the Cope rearrangement.

Although outside the central theme, the failure of 5 to be formed directly from 3 to any large extent points to a large barrier between the exo series and the endo series, only the latter possessing a conformation appropriate simultaneously to the intramolecular transfer of hydrogen and the generation of a planar double bond (Figure 2). Conformations 7_{ch}^{exo} and 7_{bt}^{endo} may be compared for visualization of that difference. In cycloheptane, the comparable barrier between the two series is calculated to be 8 kcal/mol.²⁹ In the case of 7 we have made no effort to locate the transition state between the two series. The lower pathway is by way of the intermediacy of 4, from which both the exo and endo

(27) (a) Huntsman, W. D.; Solomon, V. C.; Eros, D. *J. Am. Chem. Soc.* **1958**, *80*, 5455-5458. (b) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 4184-4187. (c) Cocks, A. T.; Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc., Chem. Commun.* **1969**, 458-459.

(28) As far as can be seen from Dreiding models and non-exhaustive calculations of the type of MM2(aug), the same separation of conformations of cycloheptane²⁹ into a chair/twist-chair and a boat/twist-boat family persists in 7.

(29) Anet, F. A. L. In *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH: Deerfield Beach, FL, 1989; pp 48-50.

(30) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781-853.

(31) MM2(aug) and experimental values, in parentheses, for $\Delta_f H^\circ$ (kcal/mol): benzyl, +47.6 (47.8);^{9,32} phenylethyl, 40.3 (40.4);³³ phenylisopropyl, 34.1 (33.2);^{33,34} ethyl, 28.4 (28.7);⁵ isopropyl, 21.0 (21.0);⁵ *tert*-butyl, 11.6 (11.6).⁵

(32) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125-134. The value for the stabilization energy of the benzyl radical 13 ± 1.5 kcal/mol was obtained from the kinetic study of the reaction C₆H₅CH₂I + HI; ΔH°_{298} = 84.3 \pm 3.1 kcal/mol. A value for ΔH°_{298} of 84.6 kcal/mol was obtained by Trotman-Dickenson from the pyrolysis of ethyl- and *n*-propylbenzene studied by an aniline carrier technique (Esteban, G. L.; Kerr, J. A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1963**, 3873-3879).

(33) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.

(34) (a) Robaugh, D. A.; Stein, S. E. *Int. J. Chem. Kinet.* **1981**, *13*, 445-462. (b) Robaugh, D. A.; Stein, S. E. *J. Am. Chem. Soc.* **1986**, *108*, 3224-3229.

(35) The truism that bond formation between two radicals *after* reaching the transition states is "concerted" is not to be confused with "concert" as a factor lowering the enthalpy of activation of cyclobutane formation from a pair of olefins *below* that expected of initial generation of the enthalpic equivalent of a diradical.

Table V. Summary of Thermochemistry^a of Cope Rearrangements of Monophenyl and Diphenyl Hexa-1,5-dienes

substituted hexa-1,5-dienes	ΔS^\ddagger	ΔH^\ddagger	$\Delta_f H^\circ$ ^b	$\Delta_f H^\ddagger$	$\Delta_f H^\circ$		$\Delta\Delta H_{fr}^c$	$\Delta\Delta H_{dr}^d$
					[2R [*]] ^b	[C ₆ dr] ^b		
none ^e	-13.8	+33.5	+20.5 ^e	+54.0	+79.2 ^f	+62.3	-25.2	-8.3
2,5-(C ₆ H ₅) ₂ ^g	-20.8	+21.3	+67.7 ^b	+89.0	+128.2 ^h	+88.5	-39.2	+0.5
2-C ₆ H ₅ ⁱ	-11.3	+29.3	+44.2	+73.5	+103.7	+75.6	-30.2	-2.1
1,4-(C ₆ H ₅) ₂ ⁴⁵	-14.4	+30.1	+69.3	+99.4	+114.4 ^j	+111.5 ^k	-15.0	-12.1
3,4-(C ₆ H ₅) ₂ ^{42b}	-12.4	+24.0	+73.5 ^l	+97.5	+114.4 ^j	+113.8 ^m	-16.9	-16.3
3-C ₆ H ₅ ⁱ	-16.6	+31.6	+46.6	+78.2	+96.8	+86.9	-18.6	-8.7
2,4-(C ₆ H ₅) ₂ ⁱ	-16.9	+24.6	+70.3	+94.9	+121.3	+100.1	-26.4	-5.2

^aAll enthalpies in kcal/mol and entropies in cal/(mol deg) (eu). ^bAll heats and enthalpies of formation result from force field calculations by MM2(aug) as described in the text.²⁰ ^cEnthalpy of concert based on model of fragmentation (fr) to two radicals (2R^{*}), $\Delta\Delta H_{fr} = \Delta_f H^\ddagger - \Delta_f H^\circ[R_1^\cdot + R_2^\cdot]$. ^dEnthalpy of concert with reference to closure to corresponding cyclohexa-1,4-diyl (C₆dr): $\Delta\Delta H_{dr} = \Delta_f H^\ddagger - \Delta_f H^\circ[C_6dr]$. ^e+20.2.⁸ ^f $\Delta_f H^\circ$ [allyl] = +39.6 (for other values, see Table 9 in ref 2b). ^gThis work. ^h $\Delta_f H^\circ$ [2-phenylallyl] = +64.1, an uncertain value. ⁱDewar and Wade.^{7a-c} ^jSee text for uncertainties in cinnamyl radical; here taken $\Delta_f H^\circ$ [1-phenylallyl] = +57.2. ^kCis: +111.9. Trans: +111.5. ^lmeso: +73.8. Rac: +73.5. ^mCis: 114.3. Trans: 113.8.

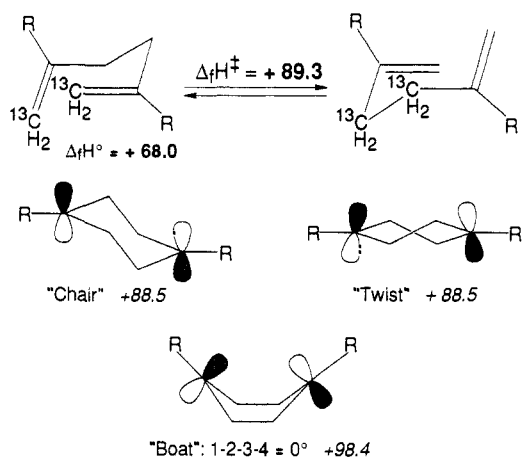


Figure 3. Three conformations of 1,4-diphenylcyclohexa-1,4-diyl (**6**, R = C₆H₅) and their respective enthalpies of formation in kcal/mol as calculated by MM2(aug). They represent possible transition structures in the degenerate Cope rearrangement of labeled 2,5-diphenylhexa-1,5-diene (**2**).

families of conformations are accessible.

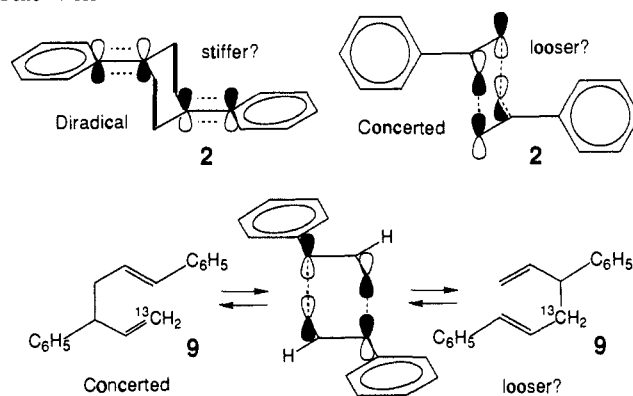
2,5-Diphenylhexa-1,5-diene (2). Beyond the fact that the enthalpy of activation for the degenerate Cope rearrangement of **2a**, $\Delta H^\ddagger = 21.3$ kcal/mol, is reliably in disagreement with the theoretical, calculated value, $\Delta H^\ddagger = 29.0$ kcal/mol,^{7e,f} a conclusion can be drawn from thermochemical quantities. The experimental value for the heat of formation of the transition state, $\Delta_f H^\ddagger$, is +89.3 kcal/mol. The corresponding theoretical value calculated by Dewar and Jie^{7e} is +101.6 kcal/mol. Its deviation from experiment, 12.4 kcal/mol, is substantial. We disagree that the discrepancy is to be dismissed as the effect of solvent, *o*-dichlorobenzene in the experiments of Dewar and Wade^{7a,b,c} and hexadeuteriobenzene in ours. More probably, the calculations miss reality by an amount large enough to smother the subtleties of mechanism being probed by placing phenyl substituents in the 2- and 5-positions of hexa-1,5-diene.

"Experimental" heat of formation, $\Delta_f H^\ddagger = +89.3$ kcal/mol, is slightly higher than those calculated by MM2(aug) for the model diradical **6**. For both the chair and the twist-boat conformations, identical heats of formation of +88.5 kcal/mol are calculated (see Figure 3). Note that the dihedral angles between the plane of the phenyl rings and the plane of the adjacent radical and its two carbon atoms are $15 \pm 1^\circ$ in both conformations. In contrast, the pure boat conformation of **6** has $\Delta_f H^\circ = +98.4$ kcal/mol (dihedral angle 17°).

The conclusion seems firm: the degenerate Cope rearrangement of **2** is not concerted in terms of the criterion of lowering of enthalpy of activation. Rather, its activation enthalpy is well predicted by estimating the enthalpy of formation of the chair conformation of 1,4-diphenylcyclohexa-1,4-diyl (**6**).

In the parent system, hexa-1,5-diene, the experimental enthalpy of activation for the degenerate Cope rearrangement is 33.5 kcal/mol.^{2a} This value contrasts with that of 42.1 kcal/mol

Scheme III



calculated from the MM2(aug) value for the chair conformation of cyclohexa-1,4-diyl ($\Delta_f H^\circ = 62.3$ kcal/mol)³⁶ and $\Delta_f H^\circ$ [hexa-1,5-diene] = 20.2 kcal/mol. The substantial enthalpy of concert, 8.6 kcal/mol, may be compared to the absence of concert in the 2,5-diphenyl analogue **2**. As previously predicted,^{4a} the phenyl groups have worked by lowering the enthalpy of activation of the hypothetical, diradical mechanism, not observed in the parent, by 20.8 kcal/mol (42.1 to 21.3 kcal/mol).

Consideration of entropies of activation lends some support to the asserted change in mechanism. For 2,6-diphenylhepta-1,6-diene (**3**), 2,5-diphenylhexa-1,5-diene (**2**) and hexa-1,5-diene, entropies of activation of -23.7, -20.8, and -13.8 eu, respectively, have been found.^{2,37} O'Neal and Benson³⁹ have shown that the entropy of activation of six-centered, thermal rearrangements from acyclic educts is inherently unfavorable because vibrational modes of low frequency are stiffened by the cyclic constitution of the transition state. Several examples reveal $\log A = 11.5 \pm 1.5$. That **3** should have a lower entropy than **2** is consistent with its having one more methylene group.

That both **2** and **3** should fall significantly below the "normal" range is, we propose, the reflection of enhanced rigidity enforced on the phenyl groups when they participate in coplanarity-requiring, benzylic stabilization. The consequent increase in frequency of the torsional modes from low in the starting olefin to

(36) $\Delta_f H^\circ$ [cyclohexa-1,4-diyl] = 62.3 kcal/mol also results from the addition of twice the increment, $\Delta\Delta_f H^\circ[(CH_3)_2CHH/(CH_3)_2CH^\cdot] = +45.9$ kcal/mol, to $\Delta_f H^\circ$ [cyclohexane] = -29.5 kcal/mol.⁸

(37) Much attention has been given to the high entropy of activation (-3.0 ± 3.0 eu) reported by Goldstein and Benson³⁸ for the "boat" Cope rearrangement of 1,5-hexadiene. An explanation for the higher enthalpy of activation for the "leakage" process that accommodates the entropy dilemma invokes an alternative cyclization of 1,5-hexadiene to the cyclopentylmethyl diradical. Its calculated $\Delta_f H^\circ$ by MM2(aug), 66.3 kcal/mol, compares with the reported heat of formation of the transition state, 65 ± 2 kcal/mol.³⁸ The conversion of one methylene group, rigidly constrained in a vinyl group, to a methylene radical, essentially free to rotate, would accommodate the observed, much more favorable entropy of activation.³⁹

(38) Goldstein, M. J.; Benson, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7147-7149.

(39) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1967**, *71*, 2903-2921.

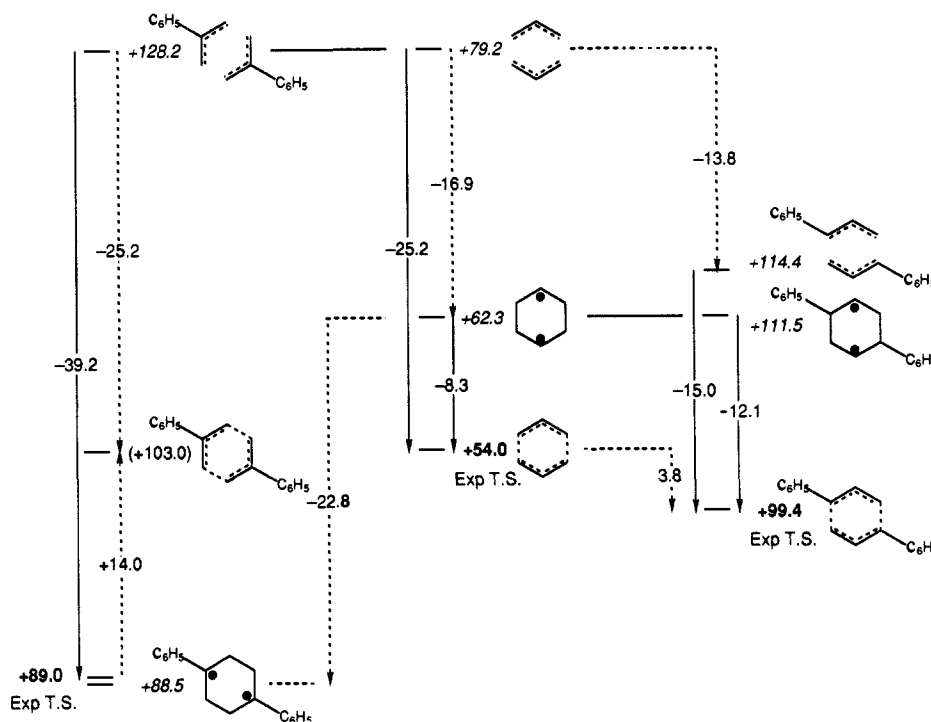


Figure 4. Enthalpies of formation in kcal/mol of experimental transition states (bold face), enthalpies of formation of radical and diradical models calculated by MM2(aug), and one assumed concerted transition state (+103.0) for the rearrangement of 2,5-diphenylhexa-1,5-diene (**2**), hexa-1,5-diene, and 1,4-diphenylhexa-1,5-diene (**9**).

much higher in the cyclic transition state leading toward the diradical affords a likely explanation of the observed decrease in entropy of activation (see Scheme III). Were the transition state concerted, "aromatic", little effect on "stiffness" of the phenyl groups would be expected, attached as they are to nodal positions. We suggest this phenomenon, an exceptionally low entropy of activation when phenyl engages in stabilization of a radical,^{40,41} as an addition to the few diagnostic tools available for discrimination between concerted and diradical mechanisms.

Thermochemical properties of mono- and diphenylhexa-1,5-dienes have been collected in Table V. Experimental parameters are supplemented by force field calculations using MM2(aug) values for heats of formation of starting dienes, appropriate radicals, and cyclohexa-1,4-diyls with a view to generating enthalpies of concert. Uncertainties vary from example to example and are unquestionably greater than that implied by the practice of not rounding before the decimal. Small differences between some of the values in the table and related values given in the text stem from the use of only calculated values in Table V.

Even though enthalpy of concert is a hybrid of *experimental* enthalpy of activation and, more often than not, *conjectured* enthalpy of formation of models of non-concerted transition states (and thereby falls exactly into the same category of concepts that encompasses enthalpy of resonance (π -electron delocalization) and enthalpy of strain), it serves as the only criterion of concert that is relatable to experiment. In this crucial way, it is distinguished from circularly theoretical criteria such as synchronicity and bond lengths in transition structures, or a baseless criterion like stereochemistry in accord with Woodward-Hoffmann rules (stereochemistry in discord serves as a reliable criterion of non-concert, loosely "forbidden").

A closer examination of **2** is facilitated by the construction in Figure 4 of a partial diagram of the relation among enthalpies

given in Table V. The point of reference is reasonably taken as the enthalpies of two allyl radicals because of the theoretically valid assumption that π -electron delocalization in nodally disposed, 2-phenylallyl is the same as in the unsubstituted allyl. The central portion visualizes the two enthalpies of concert for hexa-1,5-diene: the one, the discrepancy between actual transition state (TS) and the dissociative model of two separated allyl radicals ($\Delta\Delta H_{fr} = -25.2$ kcal/mol: the other, the discrepancy between TS and the associative, cyclohexa-1,4-diyl model (-8.3 kcal/mol).

The left-hand portion pertaining to **2** reveals clearly a striking change in mechanism. The phenyl groups can be assumed not to interact at the do-nothing nodal positions in the allyl radical and the now hypothetical concerted, "aromatic" transition state.⁴² By introducing benzylic resonance to cyclohexa-1,4-diyl, the phenyl groups invert the order of stability in the amount of -22.8 kcal/mol. Thus, the diradical mechanism falls below the dissociative mechanism by an astonishing -39.2 kcal/mol and below the unobserved, concerted transition state by 14.0 kcal/mol.

3,4-Diphenylhexa-1,5-diene (8). In a somewhat neglected study, Lutz and his co-workers⁴³ have found that *dl* and *meso* 3,4-diphenylhexa-1,5-diene (**8**) do not rearrange to 1,4-diphenylhexa-1,5-diene, as claimed by Koch,⁴⁴ but rather to the 1,6-diphenylhexa-1,5-dienes, with the following activation parameters, $\Delta H^\ddagger = +24.0 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = -12.4 \pm 0.6$ eu ($T_{av} = 100$ °C). Thus, the two phenyl groups in **10** have lowered the enthalpy of activation by 4.8 kcal/mol per phenyl vis-à-vis H, which is only slightly less than the lowering in **2** (6.1 kcal/mol). This observation is the more striking because of the wide-spread belief that radical-stabilizing substituents in the 1-, 3-, 4-, and 6-positions should have little effect on the energetics of the concerted Cope rearrangement (and no effect on the hypothetical cyclohexa-1,4-diyl mechanism). But for a reservation inherent in the considerable thermodynamic bias toward the product, the Lutz example would call into serious question the assumptions fundamental to the Dewar and Schmid approaches.^{6,7}

(40) Rearrangements of 2,5-dicyano-3-methylhexa-1,5-diene to (*Z*)- and (*E*)-2,5-dicyano-1-methylhexa-1,5-diene are reported to have unexceptional entropies of activation of -14.2 and -15.8 eu, respectively.^{6c} Nonetheless, the authors note this slight lowering and attribute it to a stiffening in the resonance-stabilized transition state.³⁹

(41) Note that, of two compounds studied by Kessler and Ott,⁴² 2,6-diphenylbicyclo[5.1.0]hepta-2,4-diene supports the hypothesis, whereas 3,7-diphenyltricyclo[3.3.1.0^{2,8}]nona-3,6-diene does not.

(42) Kessler, H.; Ott, W. *J. Am. Chem. Soc.* **1976**, *98*, 5014-5016.

(43) (a) Lutz, R. P.; Bernal, S.; Boggio, R. J.; Harris, R. O.; McNicholas, M. W. *J. Am. Chem. Soc.* **1971**, *93*, 3985-3990. (b) Lutz, R. P.; Berg, H. A. *J. Org. Chem.* **1980**, *45*, 3915-3916.

(44) Koch, H. P. *J. Chem. Soc.* **1948**, 1111-1117.

This example can be scrutinized further by estimating the enthalpy of concert for the dissociative-recombinative process involving cleavage to two free allyl radicals ($\Delta\Delta H_{fr}$) and the associative process involving the continuous or intermediary diradical, the corresponding cyclohexa-1,4-diyl ($\Delta\Delta H_{dr}$). Because there is no value in the literature for stabilization energy in the 1-phenylallyl (cinnamyl) radical,³³ the extent to which its extra resonance energy lowers the enthalpy of the concerted transition state cannot be assessed with as much accuracy as this fascinating point deserves. We arbitrarily take a value 1.5 times the stabilization energy of the benzyl radical (-12.9 kcal/mol) although Robaugh and Stein suggest an incremental stabilization of 5.4 kcal/mol.^{34b} (Geometrical isomerization in 3-(3'-phenylcyclohexenylidene)-1-phenylcyclohexane is currently under investigation.)

Relative to the dissociative, two-radical model of the rearrangement, the enthalpy of concert, $\Delta\Delta H_{fr}[8] = -16.9$ kcal/mol, is less than that of the parent hexa-1,5-diene, $\Delta\Delta H_{fr} = -25.2$ kcal/mol, by 8.3 kcal/mol (within the severe limitations imposed by the assumed enthalpy of formation of cinnamyl). Relative to the associative model, *dl*-2,3-diphenylcyclohexa-1,4-diyl, the enthalpy of concert, $\Delta\Delta H_{dr}[8] = -16.3$ kcal/mol, is greater than that of hexa-1,5-diene, $\Delta\Delta H_{dr} = -8.3$ kcal/mol. Thus, 3,4-diphenylhexa-1,5-diene emerges as strongly concerted relative to both models of non-concert. Because quantum chemistry as applied to organic chemistry finds its most important challenge in the prediction of activation parameters for concerted reactions, calculation of enthalpies of activation of this example and others that show a large enthalpy of concert vis-à-vis the diradical model, if they could be performed with "chemical" accuracy, would be welcome.

1,4-Diphenylhexa-1,5-diene (9). As noted above, conclusions drawn from the experimental enthalpy of activation of the Lutz compound are compromised by the exothermicity of the reaction, which we estimate to be 5.6 kcal/mol. A similar reservation pertains to 2,4-diphenylhexa-1,5-diene. Such a feedback of the heat of formation of the product might be expected to lower the enthalpy of activation of a concerted mechanism but not of an intermediate-interrupted mechanism in which the 2,3 and 5,6 bond lengths are calculated to be close to those of normal covalent bonds. Another illustration of a low enthalpy of activation possibly originating in a thermodynamic bias is provided by 1,1-dicyano-2-ethyl-3-methylhexa-1,5-diene ($\Delta H^\ddagger = 21.8$ kcal/mol; $\Delta S^\ddagger = -11.1$ eu).⁴⁵ In general, feedback of thermodynamic information in the product may be suggested as yet another criterion for discrimination between intermediate-interrupted and concerted mechanisms.

The compound of choice for elucidation of the effect of 1- and 4-substituents and comparison with the rearrangement of 2,5-diphenylhexa-1,5-diene (2) should be free of thermodynamic bias. An example is provided by the cursorily studied,⁴⁶ degenerate 1,4-diphenylhexa-1,5-diene (9). Determination of the activation parameters for its thermal rearrangement has furnished preliminary results⁴⁷ that reveal $\Delta H^\ddagger = 30.1 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = -14.4 \pm 1.8$ eu as the activation parameters. The unexceptional value of the entropy of activation is in concord with the prediction that little resonance-stabilizing demand should be made on phenyl in a concerted transition state (Scheme III). Enthalpy of concert with reference to dissociation to two cinnamyl radicals remains high (-15.0 kcal/mol) as does enthalpy of concert in respect of association to 2,5-diphenylcyclohexa-1,4-diyl (-12.1 kcal/mol).

The diagram of enthalpies in the instance of 9 is made more informative by placing the appropriate cyclohexa-1,4-diyls at the same reference levels. From Figure 4 (right-hand diagram), the

major effect of the phenyl groups is seen to bring the dissociative mechanism to essentially the same level (+114.4 kcal/mol) as that of the associative mechanism (+111.5 kcal/mol). Enthalpy of concert vis-à-vis the former is now -15.0 kcal/mol, 10.2 kcal/mol less than the parent, owing to the extra enthalpy of stabilization in the cinnamyl radicals. Vis-à-vis the diradical mechanism, enthalpy of concert is -12.1 kcal/mol, 3.8 kcal/mol more than it is in the parent. It is simplest to ascribe the lowering to the persistence of a small amount of cinnamyl stabilization in the concerted, aromatic transition state. How these parameters change at the next stop, 1,3,4,6-tetraphenylhexa-1,5-diene, along the way to the stable radical, 1,1,3,3-tetraphenylallyl,^{47b} is of interest.

Amusingly, perhaps provocatively, simple additivity serves to accommodate, within experimental uncertainties, the enthalpies of concert in the remaining non-degenerate examples in Table V.⁴⁸ Thus, the value $\Delta\Delta H_{fr} = -18.6$ kcal/mol for 3-phenylcyclohexa-1,5-diene is well mimicked by a model combining equal parts of the parent, $\Delta\Delta H_{fr} = -25.2$ kcal/mol, and 1,4-diphenylhexa-1,5-diene, $\Delta\Delta H_{fr} = -15.0$ kcal/mol: $[-25.2 + (-15.0)]/2 = -20.1$ kcal/mol. Similarly, $\Delta\Delta H_{dr} = -8.7$ kcal/mol is approximated by $[-8.3 + (-12.1)] = -10.2$ kcal/mol.

More remarkable is the success of additivity in handling 2-phenyl- and 2,4-diphenylhexa-1,5-diene as hybrids of one parent marked by a concerted, "aromatic" mechanism and the second by a diradical, cyclohexa-1,4-diyl mechanism. Thus, the value $\Delta\Delta H_{fr} = -30.2$ kcal/mol shown by 2-phenylhexa-1,5-diene is approximated by $[-25.2 + (-39.2)]/2 = -32.2$ kcal/mol and the value $\Delta\Delta H_{fr} = -26.4$ kcal/mol for 2,4-diphenylhexa-1,5-diene is reproduced by $[-15.0 + (-39.2)]/2 = -27.6$ kcal/mol. Similarly, for 2-phenyl- and 2,4-diphenyl-, $\Delta\Delta H_{dr} = -2.1$ and -5.7 kcal/mol can be approximated: $[-8.3 + 0.5]/2 = -3.9$ kcal/mol and $[-12.1 + 0.5]/2 = -5.8$ kcal/mol, respectively.

The notion that a transition state can comprise mechanistically different models is not to be pursued by qualitative arguments, but rather by quantum mechanical calculations that allow full optimization of geometry.⁴⁹ To be tested is the plausibility of hybrid bonds that are approximated as sp^3 - p bonds and are intermediate in length between the long bonds of the concerted transition states and the short bonds of the diradical as transition state.

Conclusions

In our current view of not-obviously-concerted thermal rearrangements, one spectrum of mechanisms is based on lifetimes of conjectural diradicals: at lifetimes too short relative to vibrational or internal rotational frequencies to be operationally distinguishable from a transition state is the hypothetical "continuous diradical" or "diradical-as-transition-state". The paradigms of the "continuous diradical" may well be thermal cis-trans isomerization of olefins and configurational rearrangement of cyclopropanes.^{4a}

As lifetimes become longer owing to unavoidable conformational barriers that protect the diradical from instantaneous collapse, the diradical becomes an intermediate having an enthalpy of formation below that of the experimental enthalpy of activation and may be more or less easily detectable, depending on the magnitude of the life-giving enthalpic barriers and the sensitivity of the method of trapping or spectroscopic observation. Cyclobutanes already seem to be ambiguous owing to the accessibility,

(48) For a thoughtful approach to the effect of substituents in 3,3-sigmatropic rearrangements in terms of free energies of formation of reactants and the two non-concerted models, see: Gajewski, J. J.; Gilbert, K. E. *J. Org. Chem.* **1984**, *49*, 11-17.

(49) Striking progress is being made toward a resolution at the theoretical level of the "biradicaloid" versus "aromatic" nature of the transition state of the rearrangement of hexa-1,5-diene and its 1,4- and 2,5-dicyano derivatives: Morokuma, K.; Borden, W. T.; Hrovat, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 4474-4479; Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213-226; Hrovat, D. A.; Borden, W. T.; Vance, R. L.; Rondan, N. G.; Houk, K. N.; Morokuma, K. *J. Am. Chem. Soc.* **1989**, *111*, submitted (and generously provided to us in preprint by Professor Borden); Bearpeak, M.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1989**, *111*, submitted.

(45) Foster, E. G.; Cope, A. C.; Daniels, F. *J. Am. Chem. Soc.* **1947**, *69*, 1893-1896.

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(47) (a) Doering, W. von E.; Birladeanu, L.; Sarma, K. S. Preliminary results; to be published elsewhere. (b) Ziegler, K. *Liebigs Ann. Chem.* **1923**, *434*, 34-78.

Table VI. Kinetic Data for Thermal Isomerization of 2,6-Diphenylhepta-1,6-diene (3) and 1,5-Diphenylbicyclo[3.2.0]heptane (4) in *o*-Dichlorobenzene

<i>t</i> , s	percent of				%	<i>t</i> , s	percent of				%
	3	4	5	others			3	4	5	others	
194.4 ± 0.3 °C											
0	99.91	0.00	0.00	0.09	(100.00)	0	0.00	99.52	0.00	0.48	(100.00)
31 380	92.97	6.21	0.12	0.71	98.78	31 380	4.42	94.43	0.30	0.85	99.54
59 040	87.77	11.02	0.22	0.99	98.08	59 040	7.89	90.68	0.55	0.88	99.08
93 540	82.89	15.92	0.43	0.76	110.49	93 540	11.50	86.09	0.83	1.58	99.02
131 880	78.16	20.66	0.58	0.59	102.06	131 880	14.83	82.94	1.08	1.15	98.48
171 540	73.40	24.92	0.76	0.91	102.82	171 540	18.11	79.17	1.35	1.37	96.02
2 308 380	37.75	45.69	13.16	3.40	106.20	2 308 380	37.66	45.71	14.75	1.87	96.13
207.3 ± 0.3 °C											
0	99.91	0.00	0.00	0.09	(100.00)	0	0.00	99.52	0.00	0.48	(100.00)
9 960	94.56	4.73	0.10	0.61	98.51	9 960	4.55	93.74	0.32	1.39	100.40
21 000	89.83	9.40	0.25	0.52	97.32	21 000	9.15	89.25	0.64	0.96	101.31
33 060	85.77	13.23	0.44	0.57	98.97	33 060	13.02	84.93	0.93	1.11	99.91
46 440	81.38	17.24	0.59	0.79	101.65	46 440	17.21	80.48	1.26	1.05	98.21
60 900	77.54	21.09	0.74	0.63	109.83	60 900	21.05	76.10	1.62	1.24	94.06
782 760	45.44	39.75	11.55	3.26	104.15	782 760	44.40	39.40	13.67	2.53	93.59
220.3 ± 0.4 °C											
0	99.91	0.00	0.00	0.09	(100.00)	0	0.00	99.52	0.00	0.48	(100.00)
3 960	95.25	3.96	0.08	0.71	99.24	3 960	5.13	93.42	0.36	1.09	99.61
9 480	90.53	8.84	0.26	0.38	99.84	9 480	11.57	86.59	0.85	1.00	99.99
13 320	87.35	11.54	0.70	0.70	100.65	13 320	15.19	82.18	1.14	1.49	98.03
18 660	83.43	15.24	0.53	0.80	99.37	18 660	21.04	76.12	1.66	1.18	97.63
25 140	79.02	19.02	0.76	1.20	100.99	25 140	26.32	70.56	2.11	1.01	97.03
354 300	48.25	31.61	16.00	4.14	102.45	354 300	47.40	31.49	17.44	3.66	86.51
234.8 ± 0.2 °C											
0	99.91	0.00	0.00	0.09	(100.00)	0	0.00	99.52	0.00	0.48	(100.00)
1 920	94.05	4.60	0.10	1.24	97.30	1 920	7.29	90.50	0.55	1.65	98.66
3 120	91.99	7.10	0.24	0.66	97.97	3 120	12.39	85.49	0.92	1.19	112.13
4 380	88.81	9.68	0.37	1.15	96.65	4 380	16.59	80.53	1.32	1.56	96.83
5 880	86.39	11.87	0.46	1.27	96.46	5 880	21.56	75.15	1.71	1.58	96.91
7 500	84.13	14.38	0.65	0.84	99.95	7 500	26.31	69.85	2.16	1.69	96.67
9 300	81.08	16.77	0.83	1.33	98.26	9 300	31.03	64.15	2.66	2.16	94.87
107 160	56.15	27.32	13.14	3.40	96.81	107 160	53.20	26.18	16.26	4.36	88.57
243.3 ± 0.1 °C											
0	99.91	0.00	0.00	0.09	(100.00)	0	0.00	99.52	0.00	0.48	(100.00)
1 500	93.09	5.67	0.22	1.02	98.52	1 500	11.29	86.00	0.91	1.80	98.69
2 100	91.02	7.56	0.27	1.16	97.09	2 100	15.53	81.47	1.26	1.74	95.09
2 760	88.82	9.47	0.37	1.34	98.03	2 760	20.15	76.31	1.64	1.90	94.77
3 480	86.68	11.50	0.50	1.32	98.39	3 480	24.00	71.73	2.00	2.27	97.66
4 260	84.54	13.30	0.70	1.47	90.69	4 260	28.10	66.95	2.41	2.54	94.00
5 040	83.76	14.80	0.77	0.66	97.97	5 040	32.73	63.27	2.79	1.21	102.11
58 500	60.23	23.97	12.99	2.81	99.77	58 500	56.87	22.91	16.51	3.70	84.07

over a small barrier, of an antiperiplanar conformation of the diradical and the working of Woodward–Hoffmann rules against concerted cleavage. In the “frustrated” Cope rearrangement (3 to 4) of this paper, the several conformational potholes in the energy surface remove one even further from the continuous diradical, to a point where one’s mouth waters in anticipation of a successful trapping. By contrast, 2,5-diphenylcyclohexa-1,5-diene (2) rearranges by a diradical mechanism close to the continuous diradical end of the spectrum.

As achievement of the goal of quantum mechanical theory in organic chemistry, the ability to calculate within ±1 kcal/mol or better enthalpies of formation of any arrangement of a chemically reasonable number of atoms, seems to remain out of reach for the indefinite future, the importance of developing pro tempore, working hypotheses and protocols for dealing with the multivariate problems of organic chemistry remains only slightly diminished. Conceptual schemes that guard against gross error, such as enthalpy of resonance, strain, and concert, serve critically in helping to bring order out of chaos. Once advancing theory has achieved control, then these previously indispensable concepts fade and are subsumed. In the interim, in the realm of origin of activation parameters, the concept of enthalpy of concert serves the mechanistic organic chemist in delineating the portion of chemical space controlled by the Woodward–Hoffmann construct, in maneuvering in non-concerted chemical space and in providing quantitative data, in the reproduction of which the success of theory is judged. In

the interim, force field calculations serve as useful repositories of thermochemical uniformities and quantitative evaluators of enthalpies of strain.

Experimental Section

NMR spectra are measured in solution in chloroform or per-deuteriobenzene on Bruker AM-300 and AM-500 instruments and are reported in ppm (δ) from TMS. Mass spectra are recorded on a Kratos MS 50 instrument. Infrared spectra are recorded on a Perkin-Elmer Model 337 grating spectrophotometer and are reported in cm^{-1} .

Analytical GLC is effected on a Hewlett-Packard 5890A instrument with a Hewlett-Packard 3393A recorder/digital integrator and a J and W Scientific DB1 column: 0.53 mm i.d. \times 30 m, film thickness 1.5 μm (column A). Preparative GLC is performed on a Varian Aerograph Model A-90-P3 instrument with a 0.25 in. \times 3 m, 5% OV 225 on Ana-chrom 60–80 mesh column (column B).

2,6-Diphenylhepta-1,6-diene (3). This compound is prepared from glutaric acid following the procedure of Marvel and Gall¹² (for more detail, see ref 11, pp 275–276): NMR 7.2 (m, 10 H), 5.26 (d, 2 H, $J = 1.8$ Hz), 5.03 (d, 2 H), 2.5 (t, 4 H, $J = 8$ Hz), 1.6 (quintet, 2 H); IR (film) 3080, 3060, 3030, 2940, 1630, 1495, 1450 cm^{-1} . For catalytic hydrogenation, 3 is recrystallized from 95% ethanol at -30 °C: mp 14.5–15.0 °C.

1,5-Diphenylbicyclo[3.2.0]heptane (4). A water-cooled solution of 1 g of 3 in 20 mL of benzene is irradiated by three 275-W General Electric sunlamps for 72 h. Concentration affords a sticky solid, crystallization of which from methanol gives 0.41 g of colorless needles: mp 74.0–74.2 °C (reported¹³ mp 72.5–73.0 °C); NMR 7.0 (m, 10 H), 2.5–2.0 (m, 10 H); IR (CCl_4) 3080, 3060, 3020, 2950, 2920, 1550, 1250 (br) cm^{-1} .

An alternate synthesis, accomplished by Courtot,¹³ is repeated here. It should be noted that under the reported conditions (135 °C for 4 min), the yield in the dehydration of 1,4-diphenylcyclohepta-1,4-diol to 1,4-diphenylcyclohepta-1,3-diene is negligible, but becomes 15–50% at 130–160 °C for periods up to 12 min (see ref 11, pp 277–280, for more detail).

The two samples of **4** have identical R_f values, the same t_R on column B, identical NMR and IR spectra, and the same melting point (mixture melting point undepressed).

Thermal Interconversion of 3 and 4. From the reaction mixture that results when a decalin solution of **3** (0.4% w/v) containing diphenylamine (0.2% w/v) is sealed under vacuum in lead-potash (Corning Glass 0120) and heated 8 h at 225 °C in a tube-furnace, **3** (65%) and **4** (35%) are the sole products, identified by GC on column B. Isolated by preparative GC on column C, **3** is found to be homogeneous by NMR and GC analysis on column A.

When a sample of **3** is heated similarly in tetralin containing diphenylamine, **4** (13%) may be isolated by GC and shown by mixture mp, tlc, GLC retention time, and NMR and IR spectroscopy to be identical with **4** produced photochemically.

1,5-Diphenylcycloheptane (5). Aliquots of a solution of 0.2 g of **3** (purity 99.8%) in 20 mL of *o*-dichlorobenzene are sealed under vacuum in two lead potash (Corning 0120) glass tubes and heated in the vapors of boiling naphthalene (220.3 °C) for 401 h. The crude reaction mixture consists of 31.0% **3**, 18.2% **4**, 47.0% **5**, and 3.8% impurities. Removal of solvent by evaporative distillation and separation of the residue by preparative GLC (column B, 200 °C, He 29 psi; t_R 6, 8, and 16 min, respectively) gives 99.8% pure 1,5-diphenylcycloheptene as determined by analytical GLC (column A, 190 °C, He 10 psi, t_R 22.5 min): m/e 248.18, calcd for $C_{19}H_{20}$, 248.37; 1H NMR (500 MHz, $CDCl_3$) 1.55 (m, 1 H), 1.64 (m, 1 H), 1.92 (m, 1 H), 2.02 (m, 1 H), 2.36 (m, 1 H), 2.46 (m, 1 H), 2.69 (m, 1 H), 2.77 (m, 1 H), 2.84 (m, 1 H), 6.17 (m, 1 H), 7.19 (m, 4 H), 7.29 (m, 4 H), 7.36 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) 28.07 (t), 31.72 (t), 34.13 (t), 50.92 (d), 125.59 (d), 125.91 (d), 126.42 (d), 126.77 (d), 128.19 (d), 128.39 (d), 129.82 (d), 144.35 (s), 144.75 (s), 148.59 (s).

Decoupling experiments strongly support structure **5** for the diphenylcycloheptene. Because the multiplets at 2.46 (e-H3) and 2.36 (a-H3) ppm are changed to dd and t, respectively, upon irradiation of the olefinic proton at 6.17 (H2), they comprise an adjacent methylene group. When these same protons (2.46 and 2.36 ppm) are irradiated, the coupling pattern of peaks at 1.92 (e-H4) and 1.55 (a-H4) is changed significantly in accord with these two protons comprising a methylene group adjacent to the first methylene group.

Irradiation of either the 1.92 or the 1.55 peak transforms the finely split triplet (tt) at 2.84 ppm (H5) into a triplet of finely split doublets and finely split doublets (dt), respectively. H5 is thus identified as a methine proton. When H5 is irradiated, multiplets at 2.02 (e-H6) and 1.92 (e-H4) are changed to dd, while those at 1.64 (a-H6) and 1.55 (a-H5) are changed to broad triplets. Finally, irradiation of these peaks at 2.02 and 1.92 transforms the coupling patterns of 2.77 (e-H7) and 2.69 (a-H7) to broad doublets.

Thermal Rearrangement of 1,5-Diphenylcycloheptene (5). A degassed 1% solution (w/v) of **5** (purity 99.8%) in *o*-dichlorobenzene is heated in a sealed ampule of lead-potash (Corning 0120) glass at 219.1 °C for 111.5 h. The crude reaction mixture consists of 84.8% **5**, 3.9% **3**, 0.8% **4**, and 10.5% various unidentified impurities (ca. 12 peaks).

Repetition with the addition of 4 molar equiv of 9,10-dihydroanthracene gives a mixture consisting of 80.6% **5**, 2.5% **3**, 1.7% **4**, and 15.2% impurities.

Kinetics of Thermal Isomerization of 3 and 4. Aliquots of stock solutions (50 μ L) of recrystallized **3** and **4** in *o*-dichlorobenzene (0.1% w/v) containing adamantyl nitrile, ACN (0.05% w/v), as internal standard are introduced into ampules of lead-potash glass (Corning 0120, 7 mm o.d. by 10 cm), previously soaked overnight in aqueous ammonia, washed with water and acetone, and dried for 24 h at 120 °C. After the solutions are degassed by 3 freeze-thaw cycles, the ampules are sealed under vacuum (5×10^{-3} Torr).

The heating bath for samples **3** and **4** (which are heated simultaneously to improve accuracy) consists of a 1-L. round-bottomed, long-necked (5 cm o.d. \times 45 cm) flask thermally insulated by asbestos tape and cotton and fitted with a water jacket at the top. The desired temperature is provided by vapors of refluxing liquids. Prior to introduction of the ampules, the liquid (ca. 500 mL) is refluxed vigorously enough to fill the neck with its vapor. For the two highest temperatures, a modified bath equipped with a flow-back tube is used to prevent the condensed liquid from entering the heating neck. Temperature is monitored with an iron-constantan thermocouple connected to a Leeds and Northrup Model 8686 millivolt potentiometer with an ice-water reference junction. The positional temperature gradient is ± 0.1 °C; small long-term drifts

Table VII. Kinetic Data for the Reversible Cope Rearrangement of 2,5-Diphenylhexa-1,5-diene-1,6- $^{13}C_2$ (**2a**) in Benzene- d_6 to 2,5-Diphenylhexa-1,5-diene-3,4- $^{13}C_2$ (**2b**)

t , s	2a ^a	2b ^a	t , s	2a ^a	2b ^a
58.40 \pm 0.08 °C					
0	98.82	1.18	512 760	57.01	42.99
41 760	91.88	8.12	923 760	51.40	48.60
99 420	83.85	16.15	1 371 720	50.42	49.58
180 240	75.12	24.88	2 237 880	49.91	50.09
294 900	66.42	33.58			
70.08 \pm 0.04 °C					
0	98.80	1.20	1 607 400	57.58	42.42
14 340	91.40	8.60	2 812 800	51.96	48.04
33 840	82.69	17.31	4 387 200	50.32	49.68
60 180	74.55	25.45	7 230 000	50.03	49.97
93 600	66.71	33.29			
81.25 \pm 0.03 °C					
0	98.77	1.23	58 380	57.18	42.82
4 560	92.13	7.87	102 360	51.51	48.49
11 640	83.61	16.39	156 120	50.27	49.73
20 100	75.63	24.37	256 740	50.05	49.95
33 600	66.44	33.56			
94.06 \pm 0.04 °C					
0	98.87	1.13	20 160	57.13	42.87
2 160	89.31	10.69	33 960	51.61	48.39
4 560	81.48	18.52	53 280	50.24	49.76
7 260	74.29	25.71	87 840	50.02	49.98
11 640	66.18	33.82			
107.83 \pm 0.05 °C					
0	98.88	1.12	6 660	57.53	42.47
600	91.15	8.85	11 760	51.92	48.08
1 260	84.60	15.40	19 080	50.24	49.76
2 340	75.31	24.69	30 780	50.23	49.77
3 780	66.89	33.11			

^a Concentrations in %; recovery in no run was less than 99.1%.

are observed due to changes in atmospheric pressure: β -(β -methoxyethoxy)ethanol, 194.4 \pm 0.3 °C; tetralin, 207.3 \pm 0.3 °C; naphthalene, 220.3 \pm 0.4 °C; tridecane, 234.8 \pm 0.2 °C; α -methyl-naphthalene, 243.3 \pm 0.1 °C. The sealed part of the ampules is protected against thermal fracture by wrapping with Teflon.

Isomerizations of **3** and **4** are followed by analytical GLC (column A, 190 °C, He 10 psi; t_R for ACN, **3**, **4**, and **5** are 2.15, 11.72, 10.07, and 22.5 min, respectively). Peak areas are corrected for detector response factors relative to ACN (0.853 \pm 0.007 and 0.965 \pm 0.012 for **3** and **4**, respectively). Results are given in Table VI.

2,5-Diphenylhexa-1,5-diene-1,6- $^{13}C_2$ (2a). Dibenzoyl ethane (0.27 g, 1.1 mmol) and ^{13}C -methyltriphenylphosphonium iodide (1.00 g, 2.5 mmol, 99.42% ^{13}C) are allowed to react with sodium hydride (0.062 g, 2.6 mmol) in dimethyl sulfoxide following the procedure of Greenwald, Chaykovsky, and Corey.¹⁶ The crude product is purified by flash chromatography (silica gel, petroleum ether) to give 0.17 g (65%) of colorless crystals (96.9% of purity by GLC: column A, 200 °C, He 10 psi); mp 48.0–48.5 °C (lit. 48–49 °C,^{7b} 51.0–51.8 °C^{12b}) after recrystallization from methanol (99.7% of purity); 1H NMR (C_6D_6 , 300 MHz) 2.61 (t, 4 H, $J(H-C) = 2.5$ Hz), 4.96 (d, 2 H, $J(H-C) = 157.2$ Hz), 5.26 (dd, 2 H, $J(H-C) = 155.9$, 1.4 Hz), 7.05–7.18 (m, 6 H), 7.26–7.32 (m, 4 H).

In our hands, the preparation of Marvel and Gall^{12b} affords only 28% of theoretical yield.

Kinetics of Thermal Isomerization of 2a. A solution of recrystallized **2a** in hexadeuteriobenzene (2% w/v) is introduced into an ampule of lead-potash glass (Corning 0120), 4 mm o.d. \times 100 mm, which had been soaked overnight in aqueous ammonia, washed successively with water and acetone, and dried for 24 h at 120 °C. After 3 freeze-thaw cycles under vacuum, the ampule is sealed at 5×10^{-3} Torr. Heating is in a constant temperature oil bath controlled by Thermotrol Model 1053A, Hallikainen Instruments. Temperatures are measured by an iron-constantan thermocouple connected to a Leeds and Northrup Model 8686 millivolt potentiometer calibrated by an ice-water reference junction.

Recovery is determined in separate experiments with unlabeled **2**. Solutions of **2** in benzene (2% w/v) containing biphenyl (0.13% w/v) as internal standard are heated to reach equilibrium under the same conditions used in the kinetic runs. The samples are then diluted 20-fold with hexane and analyzed by HPLC (column: DuPont ZORBAX SIL 4.6 mm \times 25 cm, hexane, ISCO UA-5 absorbance detector with 254 nm

optical filter). At all temperatures, recovery is >99%.

Quantitative analysis of mixtures of **2a** and **2b** can be effected by ¹H NMR because the regions of aliphatic and vinyl absorption are sufficiently well separated on the 300-MHz instrument, owing to the large ¹H-¹³C coupling constants. Aliphatic hydrogen atoms at C3 and C4 in **2a** are a narrow triplet at 2.61 ($T_1 = 1.73 \pm 0.07$ s) whereas in **2b** they are seen as widely separated doublets at 2.40 and 2.81 ($T_1 = 1.23 \pm 0.07$ s). Conversely, the *Z* and *E* vinyl hydrogen atoms in **2a** appear as a pair of widely separated doublets at 5.00 and 5.52 ($T_1 = 1.08 \pm 0.07$ s) and 4.70 and 5.22 ($T_1 = 1.08 \pm 0.07$ s), respectively. In **2b**, they appear as the pair of narrow doublets centered at 5.27 ($T_1 = 1.80 \pm 0.07$ s) and 4.96 ($T_1 = 1.66 \pm 0.07$ s), respectively.

To ensure accuracy of integration, spectra are recorded with a pulse interval of 9.0 s, corresponding to five times the longest value of T_1 shown by the protons of interest. In practice, four areas are measured in the vinyl region by integration: I_1 , $H_Z(2a)$ at 5.52; I_2 , [$H_E(2a) + H_Z(2b)$] at 5.22 and 5.27, respectively; I_3 , [$H_Z(2a) + H_E(2b)$] at 5.00 and 4.96, respectively; and I_4 , $H_E(2a)$ at 4.77. Three areas are measured in the aliphatic region: I_5 , $H_A(2b)$ at 2.81; I_6 , $H_A(2a)$ at 2.61; and I_7 , $H_A(2b)$ at 2.40.

Correction is made for the fact that each methylene group in the starting material, dibenzoylthane, is 98.90% ¹²C and 1.10% ¹³C, whereas the methyltriphenylphosphonium ylide is 99.42% ¹³C and 0.58% ¹²C. The result is four distinct β -phenylallyl groups: *A* (¹³C-1), 98.326% and *B* (¹³C-3), 0.006% (interchangeable on Cope rearrangement); and *C* (¹³C-1, ¹³C-3), 1.094% and *D* (only ¹²C), 0.574% (neither altered on Cope rearrangement).

Ratios of **2a/2b** (A/B) are calculated in three different ways (they agree within 0.7%) and are averaged for use in the calculations of specific rate constants (the sums, [$H_Z(2a) + H_Z(2b)$], [$H_E(2a) + H_E(2b)$], and [$H_A(2a) + H_A(2b)$], are normalized to 100): (i) area $H_Z(2a) = 2I_1 = A + C$ and area $H_Z(2b) = I_2 - I_4 = B + D$, whence $A/B = (2I_1 - 1.094)/(I_2 - I_4 - 0.574)$; (ii) area $H_E(2a) = 2I_4 = A + C$ and area $H_E(2b) = I_3 - I_1 = B + D$, whence $A/B = (2I_4 - 1.094)/(I_3 - I_1 - 0.574)$; (iii) area $H_A(2a) = I_6 = A + D$ and area $H_A(2b) = I_5 + I_7 = B + C$, whence $A/B = (I_6 - 0.574)/(I_5 + I_7 - 1.094)$.

Results are given in Table VII. Rate and equilibrium constants are optimized simultaneously by the nonlinear least-squares S curve fitting of observed data to the standard kinetic equation for reversible, first-order reactions. The long-time points are not included because the amount of byproduct is no longer negligible.

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Registry No. **2**, 7283-49-0; **2a**, 72316-06-4; **3**, 27905-65-3; **4**, 94383-67-2; *endo-4*, 125024-89-7; *exo-4*, 125024-90-0; dibenzoylthane, 495-71-6; *meso*-2,5-diphenylhexane, 21451-75-2; *rac*-2,5-diphenylhexane, 21451-42-3; *meso*-2,6-diphenylheptane, 125024-87-5; *rac*-2,6-diphenylheptane, 125024-88-6; bicyclo[3.2.0]heptane, 278-07-9; 2-phenylhexa-1,5-diene, 7399-52-2; 1,4-diphenylhexa-1,5-diene, 69693-35-2; *meso*-3,4-diphenylhexa-1,5-diene, 33788-14-6; *rac*-3,4-diphenylhexa-1,5-diene, 33788-15-7; 3-phenylhexa-1,5-diene, 1076-66-0; 2,4-diphenylhexa-1,5-diene, 63779-63-5.

Factors Controlling the Synchronous versus Asynchronous Mechanism of the Cope Rearrangement

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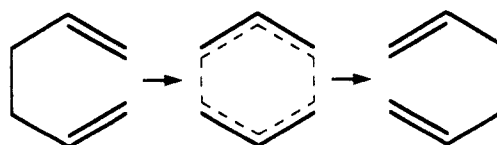
Contribution from the Dipartimento di Chimica, "G. Ciamician", dell'Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, and the Department of Chemistry, King's College, London, Strand, London WC2R 2LS, U.K. Received May 22, 1989

Abstract: MC-SCF potential surfaces for the Cope rearrangement of 1,5-hexadiene have been modeled by using a valence bond (VB) scheme parametrized with effective Hamiltonian methods. It is demonstrated that the mechanistic preference for a synchronous mechanism with an aromatic transition state versus an asynchronous mechanism with a biradicaloid intermediate is controlled by two factors: (i) the stability of the long bond in the Dewar VB structure and (ii) the softness of the Coulomb interactions between the terminal methylenes of the allylic fragments. Thus, the mechanism may be strongly affected by substituents.

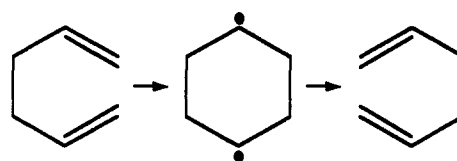
I. Introduction

There has been a controversy concerning the mechanism of the chair Cope¹ rearrangement for many years. Conflicting experimental and theoretical studies²⁻²⁰ provide evidence to support both a synchronous mechanism with an "aromatic" transition state (Scheme I) and a biradical mechanism involving a biradical intermediate (Scheme II). From a theoretical point of view, in multibond reactions it is essential to use a wave function where the possibility of biradical and aromatic transition states can be treated with a balanced level of accuracy. Thus, the MC-SCF results of Morokuma et al.²⁰ on the Cope rearrangement of the "model" reaction of 1,5-hexadiene are very convincing and provide reliable evidence that the lowest energy pathway for the model reaction is the synchronous one with the biradical intermediate

Scheme I



Scheme II



lying 22 kcal mol⁻¹ higher in energy than the synchronous transition state.

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