in the fragmentation of 2,3-diazabicyclo[2.2.1]hept-2-ene *via* a biradical intermediate.[24]

Conclusion

The Arrhenius parameters for the isomerization of 1,4-dichlorobicyclo[2.2.0]hexane to 2,5-dichlorohexa-1,5-diene have been shown to be consistent with a biradical mechanism. From the reduction in the activation energy compared to the parent hydrocarbon, a chlorine atom is shown to stabilize an α free radical by 1.5 ± 1.0 kcal/mol. This small stabilization energy is not inconsistent with stabilization energies derived from the 1-chloro-1,4-tetramethylene biradical or the α-chloroethyl radical. Rates in the liquid phase were shown to be faster than in the gas phase, with those in the less polar solvent showing the greater increase.

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(24) E. L. Allred and A. L. Johnson, *J. Amer. Chem. Soc.*, **93**, 1300 (1971).

On the Mechanism of a Diels–Alder Reaction. Butadiene and Its Dimers

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Abstract: Synthesis and kinetic study of (*R*)-(+)-1,1-dideuterio-2-(cyclohex-3-enyl)ethene (labeled 4-vinylcyclohexene) has revealed new reactions of racemization and deuterium exchange, the former of which fixes the heat of formation of *cis,trans*- (and/or *cis,cis*-) octa-3,6-diene-1,7-diyl diradical more firmly than heretofore. Redetermination of the kinetic parameters for the thermal reactions of cycloocta-1,5-diene establishes the heat of formation of the cleavage of the trans,trans (or, less probably, the cis,cis) diradical to butadiene to be 81.1 ± 2.0 kcal/mol, in good agreement with that (82.3 kcal/mol) deduced for the same reaction in the transformations of *trans*-divinylcyclobutane investigated by Hammond and DeBoer. In relation to the transition state for the Diels–Alder reaction of butadiene with itself to give 4-vinylcyclohexene, the cleavage of the diradical appears, within the present limitations of experimental results, to be somewhat higher in energy. The mechanism of this Diels–Alder reaction is tentatively concluded to be concerted, perhaps two stage, but not two step.

Controversy over the mechanism of the Diels–Alder reaction has centered on the alternatives of a one-step, concerted process and a two-step, unconcerted process.[1] The former, allowed by orbital symmetry,[2] envisages the simultaneous formation of both bonds (A),[3] whereas the latter involves the rate-determining formation of one bond, followed by a closure of the second bond more rapid than internal rotation (B).[4,5] To these widely disputed alternatives, Woodward and Katz have added a third, a merger of the two mechanisms into a two-stage process (C)[4] (Figure 1).

One generally applicable approach, particularly appropriate to the study of mechanism among thermal reorganizations, involves the placement of the interrelated isomeric elements of the system on an energy surface with a view to including or excluding certain mechanisms on energetic grounds.[5–7] Such an energy surface starts from the heats of formation of the stable components of the system and proceeds by the addition of energies of activation to define the heats of formation of the interrelating transition states. At the beginning of this work, several elements of the butadiene system had been interrelated. The data available at that time are shown in Figure 2,[8–23] which also includes apposite references.

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(1) (a) A. Wassermann, "Diels–Alder Reactions," Elsevier, Amsterdam, 1965; (b) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967); (c) H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968); (d) H. Wollweber, "Diels–Alder Reaktion," in "Methoden der Organischen Chemie," Vol. V/1c, George Thieme Verlag, Stuttgart, 1970, p 977.

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim/Bergstr., Germany, 1970.

(3) M. J. S. Dewar and R. S. Pyron, *J. Amer. Chem. Soc.*, **92**, 3098 (1970).

(4) R. B. Woodward and T. Katz, *Tetrahedron*, **5**, 70 (1959).

(5) S. W. Benson, *J. Chem. Phys.*, **46**, 4920 (1967).

(6) *E.g.*, the Cope rearrangement: W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(7) *E.g.*, the methylenecyclobutane–spiropentane system: W. von E. Doering and J. C. Gilbert, *Tetrahedron, Suppl.*, 7, 397 (1966).

(8) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970, p 142.

(9) There are three experimental values for the dimerization of butadiene to vinylcyclohexene, all determined before it was realized that *trans*-1,2-divinylcyclobutane and cycloocta-1,5-diene were among the products: E_a = 26.0,[10] 23.7,[11] and 26.8 kcal/mol.[12]

(10) W. E. Vaughan, *J. Amer. Chem. Soc.*, **54**, 3863 (1932).

(11) G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, 7, 725 (1939).

(12) D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, **10**, 198 (1951).

(13) W. Tsang, *J. Chem. Phys.*, **42**, 1805 (1965).

(14) Direct experimental values for the heats of formation of vinylcyclohexene and *trans*-1,2-divinylcyclobutane being unavailable, values are calculated from the group equivalent constants of Benson, *et al.*,[15] and an assumed increment of 1.0 kcal/mol for the interaction of a pair of cis-1,2 substituents.[16]

(15) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen,

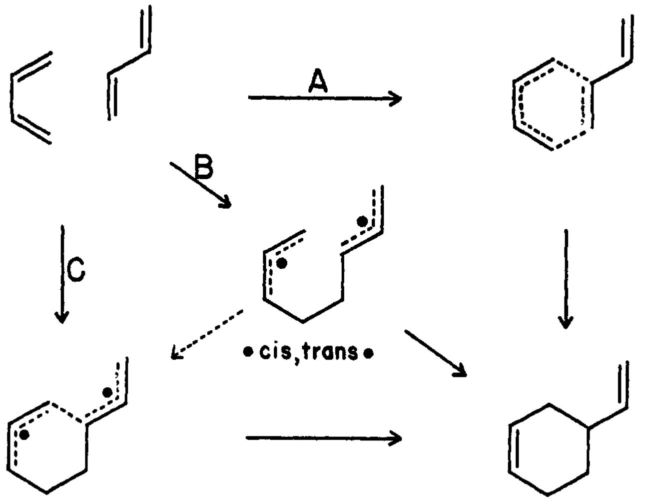

Figure 1. Outline of current hypotheses about the mechanism of the Diels–Alder reaction.

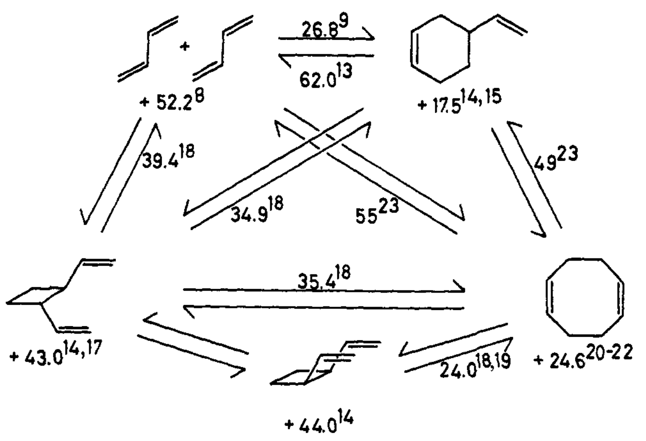

Figure 2. Five members of the C_8H_{12} system related to butadiene, each with its experimental or estimated standard heat of formation in kcal/mol and the energy of activation (E_a) by which it is related to its neighbors (where known).

If one or more of the three hypothetical octa-1,7-diene-3,6-diyl diradicals of path B (Figures 1 and 3) could be placed on this energy surface with confidence, the energy of the transition state of the Diels–Alder dimerization of butadiene might then be compared with the energy of the diradicals. Hammond and DeBoer[18] and Trecker and Henry,[24] working with the related dimethyl derivatives, have made the assumption that the rearrangements of *trans*-1,2-divinylcyclobutane to 4-vinylcyclohexene and cycloocta-1,5-diene could not be concerted and should involve two-step mechanisms proceeding over one or more of the diradicals as intermediates. The same type of two-step mechanism can be inferred for the rearrangement of cycloocta-1,5-diene to 4-vinylcyclohexene.[23] Of more importance to the structure of the transition state of the Diels–Alder dimerization, the same assumption of lack of concert can be made in respect of the decompositions of cycloocta-1,5-diene[23] and *trans*-1,2-divinylcyclobutane to butadiene.[18] These assumptions are in full accord with and, indeed, are called for by the requirements of the conservation of orbital symmetry.[2]

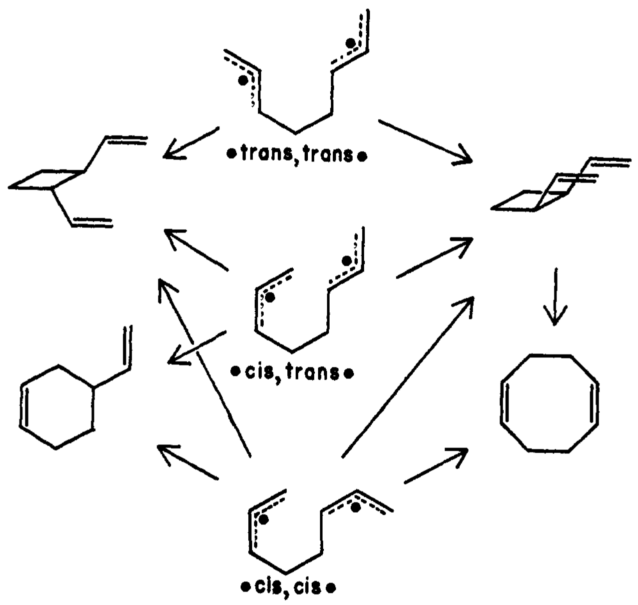

Figure 3. The hypothetical relationship of the three octa-1,7-diene-3,6-diyl diradicals to the dimers of butadiene.

Benson[5] has already compared the heats of formation of the transition states of these various reactions and has concluded that the Diels–Alder dimerization of butadiene is not a concerted process but involves an intermediate of the same heat of formation as the diradicals involved in the reference, two-step reactions. The firmness of these conclusions is weakened by several factors, such as the unavailability of experimental values for the essential heats of formation of *trans*-1,2-divinylcyclobutane and 4-vinylcyclohexene,[25] the experimental difficulties encountered in the kinetic investigations of cycloocta-1,5-diene,[27] and the uncertainties in analyzing the small amounts of butadiene formed in the decomposition of both *trans*-1,2-divinylcyclobutane[18] and cycloocta-1,5-diene.[23]

Were it possible to generate an octa-1,7-diene-3,6-diyl diradical directly from 4-vinylcyclohexene, the reliability of a comparison with the transition state of the Diels–Alder dimerization would no longer depend on the relative accuracy of the heats of formation of butadiene and 4-vinylcylohexene.[14] The way chosen here to get a bearing on these diradicals has its roots in three works on the "Mechanism of the Diels–Alder

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H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(16) From experimentally determined equilibrium constants, it is concluded that the enthalpy difference between 2 mol of butadiene and 4-vinylcyclohexene is −35.40 kcal/mol, a value in good agreement with that (−35.1) adopted from experimental and calculated thermodynamic data: G. J. Janz and M. A. DeCrescente, *J. Phys. Chem.*, **63**, 1470 (1959).

(17) H. W. B. Reed, *J. Chem. Soc.*, 685 (1951).

(18) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

(19) E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 1 (1958).

(20) K. Ziegler and H. Wilms, *ibid.*, **567**, 1 (1950).

(21) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, and G. Waddington, *J. Amer. Chem. Soc.*, **78**, 5469 (1956).

(22) R. B. Turner, *et al.*, *ibid.*, in press.

(23) R. Srinivasan and A. A. Levi, *ibid.*, **86**, 3756 (1964).

(24) D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

(25) Benson's value of +40.8 kcal/mol for *trans*-1,2-divinylcyclobutane[5] based on earlier group equivalent values[26] becomes 43.0 when based on his more recent group equivalent values,[15] while his value of 14.8 kcal/mol for 4-vinylcyclohexene[5] becomes 17.5 kcal/mol.

(26) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

(27) Srinivasan and Levi limit the reliability of their work to three temperatures, 299.3, 313.3, and 327.3°.[23]

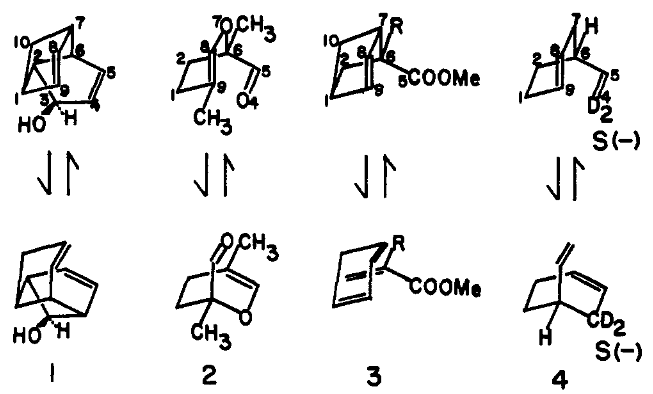

Figure 4. Efforts to detect an intermediate in the retrodiene sequence: (1) Woodward–Katz;[4] (2) Lutz–Roberts;[28] (3) Berson–Remanick;[29] (4) this paper.

Reaction" by Woodward and Katz,[4] Lutz and Roberts,[28] and Berson and Remanick.[29] In these investigations, as well as the present one, a doubly labeled product of a Diels–Alder reaction is examined for signs of otherwise concealed reactions precedent to the retrodiene or reverse Diels–Alder reaction (see Figure 4). The study of Woodward and Katz[4] brought to light a concealed reaction which was structurally of the Cope type[30] and involved rupture of the 6–7 bond and formation of the 4–9 bond. Mechanistically the reaction might have occurred by way of a concerted, six-centered Cope transition state or an intermediate bis-allylic diradical resulting from the initial rupture of the 6–7 bond. No distinction could be made between these alternatives because the presence of the one-atom bridge between C-2 and C-4 precluded rotation about the 2–6 bond.

The second example[28] lacked the C-3 bridge between C-2 and (here) O-4 and consequently was free to rotate about the 2–6 bond after a hypothetical rupture of the 6–7 bond. This study revealed a concerted Cope rearrangement of the six-centered type (or its equivalent, an intermediate bis-allylic diradical in which the rotations necessary for racemization did not occur).

The molecule studied by Berson and Remanick[29] was unable to partake of a Cope rearrangement or its equivalent, but could allow rotation about the 2–6 bond after rupture of the 6–7 bond. No hidden processes prior to the reverse Diels–Alder were revealed.

The present and fourth example was designed to permit both the Cope rearrangement and free rotation about the 2–6 bond. Although the two previous failures[28,29] to observe the consequences of rotation were discouraging, a simple estimate of the activation energy for the conversion of 4-vinylcyclohexene to its related *cis,cis-* or *cis,trans*-octa-1,7-diene-3,6-diyl diradical (•cis,cis• or •cis,trans•) provided encouragement. The starting point for the estimation is the activation energy for dissociation of ethane (88 kcal/mol). In 4-vinylcyclohexene, this process should be lowered as much as 9 kcal/mol by three alkyl substituents and 24 to 28 kcal/mol by the two allylic resonance energies.[31] The resulting estimated activation energy of 51–55 kcal/mol may be added to the calculated heat of formation of 4-vinylcyclohexene (16–18 kcal/mol)[14,16] to give a predicted heat of formation of the diradicals of 67–73 kcal/mol. Since the experimental heats of formation of the transition state of the Diels–Alder dimerization of butadiene[8,9] and its reverse[13] fall in the range 76–80 kcal/mol, there was good reason to hope of this example that an intermediate diradical would be detectable if present.

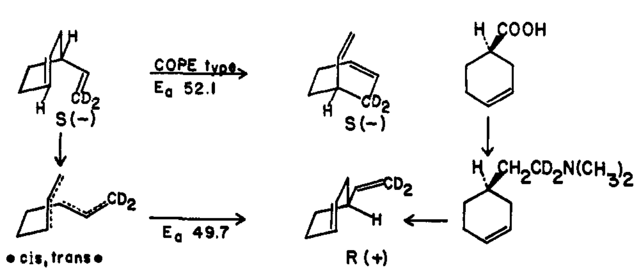

Figure 5. Outline of preparation of (*R*)-(+)-1,1-dideuterio-2-(cyclohex-3-enyl)ethene.

Several approaches to the preparation of (*R*)-(+)-2-(cyclohex-3-enyl)-1,1-dideuterioethene were explored before the sequence outlined in Figure 5 was chosen. The readily available cyclohex-3-enoic acid is conveniently resolved by way of its brucine salt.[32] In our hands the salt of the (*R*)-(+) acid appears first while the salt of the (*S*)-(−) acid can be obtained from the mother liquor. Both can be obtained in a state apparently approaching optical purity. The (*R*)-(+)-cyclohex-3-enoic acid is extended by the Arndt–Eistert sequence to *N,N*-dimethyl-(*R*)-(+)-cyclohex-3-enylacetamide into which two atoms of deuterium are now introduced in the reductive step to dimethyl-(*R*)-(+)-2-(cyclohex-3-enyl)-1,1-dideuterioethylamine. Pyrolysis of the related amine oxide furnishes optically active, deuterium-labeled 4-vinylcyclohexene [(*R*)-(+)-1,1-dideuterio-2-(cyclohex-3-enyl)ethene]. The absolute configurations, although not essential to this work, are established by Goldberg and Lam[33] by interrelationship with (*R*)-(+)-cyclohex-3-enoic acid.

Thermal reaction at 360° of optically active deuterium-labeled 4-vinylcyclohexene revealed two new reactions: loss of optical activity and rearrangement of deuterium. These reactions were accompanied by decomposition to butadiene and numerous minor products, the formation of which could not be repressed by the addition of aniline or diphenylamine, or by extensive seasoning of the 12-l. Pyrex vessel. The possibility that racemization and deuterium exchange might have resulted from the liberation and recombination of butadiene was excluded by calculation and by experiment. From the kinetic data of Duncan and Janz on the decomposition of 4-vinylcyclohexene[34] and the data of Rowley and Steiner on the dimerization of 1,3-butadiene,[12] it was calculated that an initial 50-mg quantity of 4-vinylcyclohexene in a 12-l. vessel would suffer 10.2% decomposition to butadiene at 380° for

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[28] R. P. Lutz and J. D. Roberts, *J. Amer. Chem. Soc.*, 83, 2198 (1961).

[29] J. A. Berson and A. Remanick, *ibid.*, 83, 4947 (1961).

[30] S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 684–696.

[31] See, for example, P. Nangia, and S. W. Benson, *J. Amer. Chem. Soc.*, 84, 3411 (1962).

[32] This acid has been resolved incompletely ($[\alpha]^{28}\text{D}$ −1.4° in methanol) by three crystallizations of its quinine salt from acetone.[33] This resolution is to be contrasted with the present use of brucine which affords acid of $[\alpha]^{25}\text{D}$ +109.9° in chloroform after four crystallizations.

[33] S. I. Goldberg and F. L. Lam, *J. Org. Chem.*, 31, 240 (1966).

[34] N. E. Duncan and G. J. Janz, *J. Chem. Phys.*, 20, 1644 (1952).

Table I. Average and Weighted Rate Constants and Activation Parameters for the Racemization and the Deuterium Rearrangement of (+)-4-Vinylcyclohexene-*2,2,d*$_2$

Temp, °C	$k_{\alpha,\ 365} \times 10^6$ sec^{-1}	$k_{\alpha,\ 365}{}^a \times 10^6$ sec^{-1}	$k_{\mathrm{D\ exch}} \times 10^6$ sec^{-1}	$k_{\mathrm{D\ exch}}{}^a \times 10^6$ sec^{-1}
335.0	1.83 ± 0.15	1.78 ± 0.09	2.26 ± 0.07	2.29 ± 0.04
345.0	3.46 ± 0.09	3.44 ± 0.08	4.84 ± 0.20	4.71 ± 0.15
360.6	8.53 ± 0.19	8.74 ± 0.15	11.46 ± 0.86	11.29 ± 0.82
370.0	16.42 ± 0.25	16.37 ± 0.20	24.40 ± 0.34	24.47 ± 0.37
380.1	30.53 ± 0.19	30.80 ± 0.21	45.95 ± 0.40	45.97 ± 0.43

$\log k_\alpha = (12.09 \pm 0.26) - (49{,}650 \pm 790)/2.303RT$

$\log k_{\mathrm{D}} = (13.09 \pm 0.62) - (52{,}140 \pm 1780)/2.303RT$

At 360°, for racemization, $\Delta S^{\ddagger} = -4.7$ eu and for deuterium exchange, $\Delta S^{\ddagger} = -0.1$ eu

[a] Weighted according to extent of reaction.

3 hr (the highest temperature and the longest time of reaction at this temperature employed in our studies). Of this amount, 1.2% would recombine to give necessarily racemic and exchanged 4-vinylcyclohexene, which would thus constitute only 0.13% of the material recovered in our kinetic runs. Experimental confirmation was obtained by heating 6.38 mg of butadiene at 380° for 3 hr and isolating 4-vinylcyclohexene in 1.5% of theory.

The intramolecularity of the deuterium exchange was confirmed by mass spectral analysis which revealed no tri- or tetradeuterated species.

The kinetic data were calculated on the assumptions that the racemization was first order, that the deuterium exchange was a reversible first-order reaction, and that the secondary isotope effect could be neglected. Average rate constants and rate constants weighted according to the extent of reaction are given in Table I with errors which denote the mean errors of the average. The usual Arrhenius plot was analyzed by the method of least squares and led to the activation parameters reported in Table I.

The exchange of deuterium is assumed to require the formation of •cis,cis• and its reclosure, or its concerted equivalent, a Cope rearrangement. It is important to note that rearrangement by a concerted mechanism of the Cope type would regenerate the original enantiomer and could not accommodate racemization; that is, (*R*)-(+)-2-(cyclohex-3-enyl)-1,1-dideuterioethene would rearrange to (*R*)-(+)-1-(2,2-dideuteriocyclohex-3-enyl)ethene in a reaction comparable to those previously reported rearrangements[4,28] of the Cope type (see Figure 4).

Racemization is assumed to involve •cis,cis• and/or •cis,trans• since a concerted mechanism cannot be visualized. On the strength of a slight preference discernible in models it may be assumed that •cis,trans• is formed somewhat more rapidly than •cis,cis• and that the immediate product of bond fission has the chiral (*P*)-synclinal conformation.[35] In our opinion the more economical mode of racemization involves rotation of the planar trans radical *vis-à-vis* the C_5 methylene group followed by reclosure to the axial (*S*)-(−)-4-vinylcyclohexene. Clearly an alternate mode involves rotation within the diradical to produce the achiral antiperiplanar conformation. It is intended to examine the details of the racemization and the deuterium exchange more closely by interrupting the process short of the establishment of equilibrium, oxidizing the product to 4-cyclohexenylacetic acid, separating the pure enantiomers, and determining the deuterium content of each.[36]

Since the activation energy of deuterium exchange appears to be slightly higher than the activation energy of racemization[37] and since it is entirely consistent with the dictates of the conservation of orbital symmetry[2] that racemization not occur by a concerted process, the deuterium exchange probably proceeds in a nonconcerted fashion by way of •cis,cis• and not a pseudocyclic, six-centered transition state of the Cope type.[38]

In view of the large magnitude of 23 kcal/mol estimated for the concert in the four-centered Cope rearrangement,[40] it is surprising that the element of concert seems to have been so completely overwhelmed in 4-vinylcyclohexene. One part of the explanation lies in the higher energy (≥6 kcal/mol) of the six-centered state,[6] another must be found in a lowering of energy in the diradical (•cis,cis•) by two alkyl substitutions (~4 kcal/mol), but there remains a large residue for the eradication of which the bicyclic nature of the hypothetical transition state may be responsible.

As a first step in the construction of the energy surface (see Figure 6A), the heat of formation of the transition state for deuterium exchange, which is judged to involve some combination of the Cope rearrangement and the intermediate •cis,cis•, may be placed at 69.6 ± 2.1 kcal/mol [$\Delta H_f°$(4-vinylcyclohexene) = 17.5 ± 1.0 kcal/mol[14] and $E_a(\mathrm{D_{exch}})$ = 52.1 ± 1.8 kcal/mol (Table I)]. Similarly, the heat of formation of the transition state for racemization, which is considered to involve the generation of •cis,trans•, can be placed at 67.2 ± 1.3 kcal/mol.

Although the contribution of rotational barriers to the energies of the two transition states is not known, it may be regarded as a small but essential factor in the rearrangements of cyclic compounds. The existence of this contribution is recognized by the arbitrary assignment to •trans,trans•, •cis,trans•, and •cis,cis• of values of $\Delta H_f°$ (66.0, 67.0, and 68.0 kcal/mol, re-

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(35) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

(36) This approach is similar in concept to that employed in elucidation of the racemization of thujene [W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, 27, 2005 (1971)] and could reveal the relative importance of the concerted Cope process for deuterium exchange and of •cis,cis• and •cis,trans• for racemization.

(37) It is emphasized that the difference in the activation energies is comparable to their probable errors and possibly insignificant. Note that the ratio of the rates of exchange to racemization varies within the narrow range, 1.29 at 335.0° to 1.49 at 380.1°, which, however, corresponds to $\Delta\Delta E_a$ = +2.45 kcal/mol.

(38) Berson and Jones have reached a similar conclusion about the mechanism of a structurally related rearrangement.[39]

(39) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5017 (1964).

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

spectively) which are lower than $\Delta H_f°$ of the transition states for racemization and deuterium exchange. (In lieu of a better method, the conventional procedure[5] of adding 1.0 kcal/mol for each interaction of the *cis*-butene type is followed.)

Another sighting on the $\Delta H_f°$ of the octa-1,7-diene-3,6-diyl diradical can be obtained from cycloocta-1,5-diene through its thermal rearrangement to 4-vinylcyclohexene (and butadiene; *vide infra*). This was one of two reactions relied on by Benson in his recent analysis of the Diels–Alder reaction[5] to provide fixed points for the heat of formation of the diradical in the two-step mechanism of the dimerization of butadiene. The importance of this point is increased by the availability of an experimental heat of formation for cycloocta-1,5-diene. Turner, *et al.*,[22] report its heat of hydrogenation in solution (53.7 ± 1.0 kcal/mol) to cyclooctane, for which an accurate heat of formation under standard conditions of −30.06 kcal/mol is available.[21] If a small positive correction of 1 kcal/mol for converting heats of hydrogenation in the liquid phase to the gas phase is applied, a heat of formation of cycloocta-1,5-diene of 24.6 ± 1.0 kcal/mol may be calculated and compared with the value of 22.0 kcal/mol used by Benson.[5]

The kinetics of the rearrangement of cycloocta-1,5-diene to 4-vinylcyclohexene had been investigated by Srinivasan and Levi[23] who reported an activation energy, E_a = 49 kcal/mol, but remarked that, "at 338.9 and 358.1°, the plot showed large departures from linearity at all conversions" and "in packed vessels . . ., the first-order rate constant was nearly the same at 313.2 and 338.7° but not at 358.2°." Whereas most of the difficulty encountered by Srinivasan and Levi in Pyrex vessels could be removed by the addition of a tenfold excess of aniline, the present reinvestigation of the kinetics was conducted in a 3.5-l., hand-blown vessel of lead–potash glass, which had shown itself free of radical-initiating and acid-catalyzing properties. Not only were good first-order plots obtained to 85–95% reaction, but the rate constants were somewhat smaller than comparable rate constants obtained in the Pyrex flask with aniline. The results are shown in Table II.

Table II. Weighted Rate Constants and Activation Parameters for the Thermal Reorganization (k) of Cycloocta-1,5-diene to 4-Vinylcyclohexene (k_1) and Butadiene (k_2)

Temp, °C	$k \times 10^5$ sec^{-1}	$k_1 \times 10^5$ sec^{-1}	$k_2 \times 10^5$ sec^{-1}
302.3	5.70 ± 0.14	4.58 ± 0.30	1.13 ± 0.04
317.5	18.45 ± 0.18	14.42 ± 0.54	4.00 ± 0.11
332.1	54.96 ± 0.47	42.73 ± 1.21	12.18 ± 0.23
348.5	177.26 ± 0.76	133.4 ± 4.3	44.21 ± 1.22
357.4	335.05 ± 1.51	249.7 ± 6.4	85.84 ± 1.81

$\log k = (15.99 \pm 0.23) - (53{,}290 \pm 760)/2.303RT$
$\log k_1 = (15.55 \pm 0.34) - (52{,}400 \pm 1140)/2.303RT$
$\log k_2 = (16.30 \pm 0.27) - (55{,}930 \pm 930)/2.303RT$

At 330°, $\Delta S^{\ddagger}$ for overall decomposition, +13.2 eu; for formation of vinylcyclohexene, +11.2 eu; and for formation of butadiene, +14.6 eu

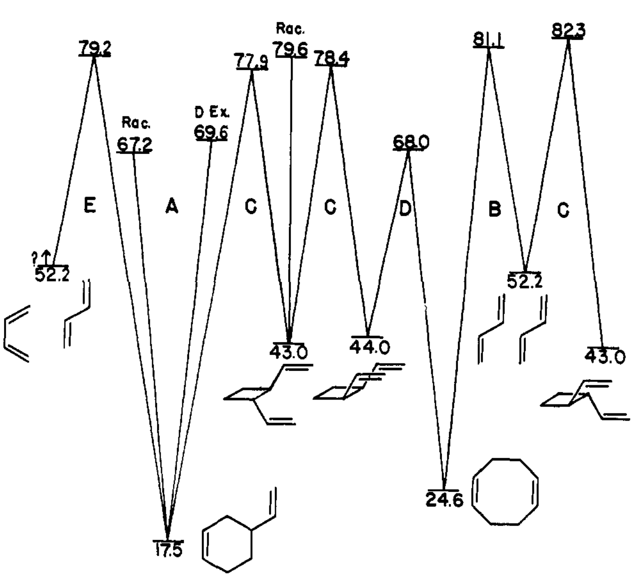

Figure 6. The energy surface shows heats of formation (kcal/mol) of isolable molecules and interconnecting transition states of (A) racemization and deuterium exchange in 4-vinylcyclohexene, (B) thermal reorganization of cycloocta-1,5-diene, (C) racemization and thermal reorganization of *trans*-1,2-divinylcyclobutane, (D) the Cope rearrangement of *cis*-1,2-divinylcyclobutane, and (E) the dimerization of butadiene to 4-vinylcyclohexene.

One plausible mechanistic path for the rearrangement of cycloocta-1,5-diene to 4-vinylcyclohexene involves the generation of •cis,cis• (see Figure 3) as the rate-determining intermediate.[5] In terms of the previous analysis of the racemization of 4-vinylcyclohexene, $\Delta H_f°$ for the transition state for the closure of the cis,trans diradical can neither be greater than 67.2 ± 1.3 kcal/mol nor appreciably greater than $\Delta H_f°$ [•cis,-trans•]. Owing to the unresolved problem of the mechanism of the deuterium exchange, it must be assumed that •cis,cis• behaves like •cis,trans• and, if formed in the rearrangement of cycloocta-1,5-diene, can be expected to close to 4-vinylcyclohexene with little or no energy of activation.

According to this mechanistic hypothesis, the heat of formation for the rate-determining transition state in the transformation of cycloocta-1,5-diene to 4-vinylcyclohexene ($\Delta H_f°$[COD → VCH] = 77.0 ± 1.5 kcal/mol: the sum of $\Delta H_f°$[COD] = 24.6 ± 1.0 kcal/mol and E_a[COD → VCH] = 52.4 ± 1.1 kcal/mol) is associated with generation of the intermediate cis,cis diradical. That this value should be so much higher than $\Delta H_f°$[•cis,trans•] ≤ 67.2 ± 1.3 kcal/mol (and presumably the cis,cis diradical as well) can be rationalized in terms of the "empirical strain" energy of cycloocta-1,5-diene.

As this problem has been analyzed by Turner, *et al.*,[22] the heat of hydrogenation of cycloocta-1,5-diene (53.7 ± 1.0 kcal/mol) closely approximated that of two molecules of the *cis*-butene type (2 × 27.4 kcal/mol). It could therefore be concluded that the diene must possess as much strain as its product of hydrogenation, cyclooctane. In reality cyclooctane reveals a significant amount of strain, whether gauged against four-thirds of cyclohexane as model, eight methylene groups from normal paraffins, or the single conformation hypothesis of Schleyer, *et al.*[41] If this "empirical strain" of cyclooctane is taken to be 9.5 kcal/mol, the "empirical strain" of cycloocta-1,5-diene is 8.4 kcal/mol.

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[41] P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

In the hypothetical closure of a strain-free cis,cis diradical to the strained cycloocta-1,5-diene most, if not all, of the strain will have been introduced by the time the transition state for formation of the carbon–carbon bond is reached. The magnitude of nonbonded interactions is not expected to be substantially affected by the stretching of any one bond and will be about as large in the transition state as in the final product. The closure of the diradical would thus be expected to have an additional activation energy comparable in magnitude to the "empirical strain" of the product, cycloocta-1,5-diene. Viewed in the reverse direction, the original strain will remain largely unrelieved at the transition state for bond breaking. Much larger changes in angle and distances are required to produce the cis,cis diradical in its strain-free conformation. It is an important consequence of this analysis that strain-free cis,cis diradicals, no matter how generated, can be expected to cyclize to 4-vinylcyclohexene much faster than to cycloocta-1,5-diene.

This analysis is at odds with that of Benson[5] who argues that the activation energy for the closure of the cis,cis diradical to cycloocta-1,5-diene (E_a[•cis,cis• → COD]) is zero "since the C_8 ring has only 5.3 kcal/mol of strain." In our analysis, this activation energy would be 7.4 ± 2.6 kcal/mol, the difference between ΔH_f°[COD → VCH] for the rearrangement of cycloocta-1,5-diene to 4-vinylcyclohexene (77.0 ± 1.5 kcal/mol) and ΔH_f°[VCH/D_{exch}] for deuterium exchange in 4-vinylcyclohexene (69.6 ± 2.1 kcal/mol). To the extent that ΔH_f°[•cis,cis•] is less than ΔH_f°[VCH/D_{exch}], E_a[•cis,cis• → COD] would be larger than 7.4 kcal/mol.[42]

The large strain in cyclooctadiene may be related causally to the strikingly high values of log A for its rearrangement to 4-vinylcyclohexene and decomposition to butadiene. Much of its strain originates in eclipsed conformations which would remain in the immediate product of bond breaking. From models, these conformations appear closely to resemble in their geometry the transition states for rotation about the carbon–carbon bond. Consequently, they can be expected to proceed immediately to the nearest staggered conformation. The effect is to make bond breaking more fruitful than it would be in vinylcyclohexene, where, for example, recyclization of the immediate product of bond breaking is not prevented either by an inevitable separating rotation or by the necessity to reintroduce strain energy. The possibility that this way of considering the thermal openings of rings may be useful in other instances is offered as justification for such a detailed analysis of a hypothetical mechanism which may be no more plausible than an alternative to be discussed below.

The set of data developed by Hammond and DeBoer[18] and by Trecker and Henry[24] must be considered before discussing the role of butadiene in the system of interrelated reactions. Those data involve *trans*-1,2-divinylcyclobutane [*trans*-DVCB] in its thermal rearrangement to 4-vinylcyclohexene [VCH] and cycloocta-1,5-diene [COD], its racemization, and its cleavage to butadiene [BD] (see Figure 2). The heat of formation of *trans*-1,2-divinylcyclobutane is not known and must be calculated.[14] The most doubtful feature of this calculation is the assumption that the strain energy of cyclobutane,[43] the only member of its class for which the quantity has been determined, aside from bicyclo[4.2.0]octane,[8] can be carried over to *trans*-divinylcyclobutane (and *cis*-; *vide infra*) without an additional uncertainty. With an explicit reservation wherever ΔH_f°[*trans*-DVCB] and ΔH_f°[*cis*-DVCB) appear in the sequel, we use the values, 43.0 ± 1 and 44.0 ± 1 kcal/mol, respectively. The relevant results of the kinetic studies of Hammond and DeBoer[18] are collected in Table III.

Table III. Kinetics of Rearrangements of *trans*-1,2-Divinylcyclobutane[a]

Disappearance:	k at 187.3° $= 3.58 \times 10^{-4}$ sec^{-1};
	$\log k = 13.12 - 34.86/\theta$
Racemization:	k_α at 187.2° $= 5.21 \times 10^{-4}$ sec^{-1};
	$\log k_\alpha = 14.29 - 36.64/\theta$
	$\text{Log}\,[k_{VCH}/k_{COD}] = 0.19 + 0.49/\theta$
	$\text{Log}\,[k_{VCH}/k_{BD}] = -1.035 + 4.45/\theta$

[a] θ is defined in $\log k = \log A - E_a/\theta$ as $(2.303)(1.987)T \times 10^{-3}$ (E_a in kcal/mol).

The major product (70%) of its rearrangement at 154° is 4-vinylcyclohexene, for the transition state of which ΔH_f°[*trans*-DVCB → VCH] = +77.9 kcal/mol[44] (see Figure 6C).

The reaction can be concerted if the new bond is formed antarafacially and with inversion of configuration. If the reaction is not concerted, •cis,cis• and •cis,trans•, but not •trans,trans•, are possible intermediates which can close to 4-vinylcyclohexene with negligible or small activation energies (see Figure 3).

The difference between the previously estimated ΔH_f°[•cis,trans•] ≦ 67.2 ± 1.3 kcal/mol and ΔH_f°[*trans*-DVCB → VCH] = +77.9 kcal/mol can be equated with the activation energy for the closure of •cis,trans• to *trans*-divinylcyclobutane: ΔH_f°[•cis,trans• → *trans*-DVCB] = +10.7 ± 3 kcal/mol]. This activation energy is uncertain in ΔH_f°[*trans*-DVCB], ΔH_f°[•cis,trans•] and the relatively unimportant omission of the cis,cis diradical from consideration. About 10 kcal/mol more strain, of the total of 26.2 kcal/mol, has been built into the system at the transition state than has been recovered at that point from the total exothermicity of the reaction (estimated to be 24.0 kcal/mol: 67.0 − 43.0). Although this type of information may be evaluated in terms of Hammond's postulate, the incorporation of an energy of 10.7 ± 3 kcal/mol into the transition state may not be interpreted to signify that the transition state is along the way to the product by a value ≧ 10.7/26.2. Rather, the sum of two functions, one relating strain and bond distance, the other bond strength and bond distance, happen to have a maximum

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[42] We assume 68.0 kcal/mol for ΔH_f°[•cis,cis•] while Benson arrives at a value of 71.6 kcal/mol by (a) equating E_a = [COD → VCH] and ΔH_f°[•cis,cis•], (b) accepting the low value for ΔH_f°[COD] = 22.0 kcal/mol instead of 24.6 ± 1.0 kcal/mol,[22] and (c) relying on the value of Srinivasan and Levi[23] of 49.6 kcal/mol for E_a[COD → VCH] (instead of 52.4 kcal/mol).

[43] S. Kaarsemaker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, 71, 261 (1952).

[44] The kinetics were measured in solution and, as pointed out by Benson,[5] are not to be compared with gas-phase parameters without explicit recognition of the uncertainty introduced. We consider it essential to reevaluate the kinetics of the rearrangement of the divinylcyclobutanes in the gas phase, but shall proceed with the analysis of the presently available results in the meantime.

owing to the more rapid increase of strain with decreasing bond distance.

A lesser portion of the rearrangement of *trans*-divinylcyclobutane (26% at 154°) proceeds to cycloocta-1,5-diene with E_a = 35.4 kcal/mol and ΔH_f°[*trans*-DVCB → COD] = +78.4 kcal/mol. If the previous conclusion is accepted that both the cis,cis and cis,trans diradicals close to the essentially strain-free 4-vinylcyclohexene much faster than to the strained cycloocta-1,5-diene [log $(k_{VCH}/k_{COD}] = (7.4 \pm 2.6)/\theta]$, the mechanism of formation of cycloocta-1,5-diene plausibly must involve the third diradical, •trans,trans•. This diradical, being sterically barred from proceeding to 4-vinylcyclohexene (see Figure 3), may either return to *trans*-divinylcyclobutane or it may close to *cis*-divinylcyclobutane[45] which undergoes relatively rapid rearrangement of the six-centered Cope type to cycloocta-1,5-diene: E_a = 24.0 kcal/mol; ΔH_f°[*cis*-DVCB → COD] = +68.0 kcal/mol[18] (based on an assumed ΔH_f°[*cis*-DVCB] = +44.0 kcal/mol; see Figure 6D).

The racemization of optically active *trans*-divinylcyclobutane has also been observed by Hammond and DeBoer and, indeed, is the fastest reaction of *trans*-DVCB even though its activation energy is higher: E_a = +36.6 kcal/mol; ΔH_f°[*trans*-DVCB/racemic] = 79.6 kcal/mol.[18] Detailed dissection of the relative rates of formation of cis,cis, cis,trans, and trans,trans diradicals and of the partition of •trans,trans• between original and enantiomeric *trans*-divinylcyclobutane and cycloocta-1,5-diene must await the results of a thorough reexamination. Meanwhile it appears plausible that racemization also involves the formation of the trans,trans diradical. The conclusion of the present work that cis,cis and cis,trans diradicals from *trans*-DVCB, either racemic or optically active, should cyclize rapidly to 4-vinylcyclohexene is consistent with the report of Hammond and DeBoer that optical activity is observed in the 4-vinylcyclohexene formed from optically active *trans*-divinylcyclobutane.[18]

Butadiene has been related to these C_8H_{12} dimers. Among the products of the thermal reaction of *cis,cis*-cycloocta-1,5-diene, Srinivasan and Levi[23] found 15–20% of butadiene between 313.3 and 327.3°, but variable amounts at lower temperature, and have calculated the activation energy to be 6.2 kcal/mol greater than the activation energy for rearrangement to 4-vinylcyclohexene.[46] In the present reinvestigation of the thermal rearrangement of cycloocta-1,5-diene, the formation of butadiene has been followed more accurately and its activation energy is reported in Table II, whence log $k_{VCH}/k_{BD} = -0.75 + 3.5/\theta$. From a plot of the ratio of 4-vinylcyclohexene to butadiene against $1/T$, the activation energy is found to be 4.1 kcal/mol greater than that of the formation of 4-vinylcyclohexene (log $k_{VCH}/k_{BD} = (-0.95 \pm 0.50) + (4.1 \pm 1.4)/\theta$). The heat of formation of the rate-determining transition state, ΔH_f°[COD → BD], is thus 81.1 ± 2.0 kcal/mol and is to be compared to ΔH_f°[COD → VCH] = 77.0 ± 1.5 kcal/mol (from Table II).

The first mechanism to be considered for the transformation of cyclooctadiene to butadiene is that of Benson in which the rate-determining step is the opening of COD to •cis,cis•, the common intermediate for the formation of 4-vinylcyclohexene and butadiene. Their ratio, 4.02 at 575.3°K, is a reflection of the preference of •cis,cis• for closure over cleavage. In the present work a question is raised about this interpretation. If one recalls that $\Delta H_f^\circ[\mathrm{VCH/D_{exch}}]$ is 69.6 kcal/mol, that ΔH_f°[•cis,cis•] is probably lower (*e.g.*, 68.0 kcal/mol), that ΔH_f°[COD → VCH] is 77.0 ± 1.5 kcal/mol, and that ΔH_f°[COD → BD] is 81.1 ± 2.0 kcal/mol, it follows credibly that $k_{VCH}/k_{BD} = 10^{\Delta A + 13.1/\theta}$, where ΔA has the improbably large value of −4.37 if k_{VCH}/k_{BD} = 4.02 at 575.3°K and is in significant discord with the experimental value of ΔA = −0.75, derivable from the data in Table II.

An alternate mechanism for the conversion of cyclooctadiene to butadiene, which may also be applied to its rearrangement to 4-vinylcyclohexene [previously discussed in terms of the direct intermediacy of •cis,cis• (*vide supra*)], involves (1) a preequilibrium between cycloocta-1,5-diene and *cis*-1,2-divinylcyclobutane (ΔH_f°[COD → *cis*-DVCB] = 68.0 kcal/mol;[18] see Figure 6D), (2) equilibration of *cis*- and *trans*-1,2-divinylcyclobutane by way of •trans,trans• (the heat of formation of the transition state of which (ΔH_f°-[*cis*-DVCB → •trans,trans•]) is equated with ΔH_f°-[*trans*-DVCB → COD] = 78.4 kcal/mol as previously outlined; see Figure 6C), and (3) production of vinylcyclohexene by way of •cis,trans• and •cis,cis• diradicals from *trans*-DVCB as previously outlined and production of butadiene by cleavage of •trans,trans•. The heat of formation of this transition state, ΔH_f°-[•trans,trans• → BD], is then equated with ΔH_f°-[COD → BD] = 81.1 ± 2.0 kcal/mol (the sum of ΔH_f°-[COD] = 24.6 ± 1 kcal/mol, E_a[COD → VCH] = 52.4 ± 1.1 kcal/mol and $\Delta\Delta E_a$[VCH/BD] = 4.1 ± 1.4 kcal/mol; see Table III and Figure 6B). In this scheme, the ratio of vinylcyclohexene to butadiene becomes the ratio of the rate of formation of •cis,trans• and •cis,cis• to the rate of formation and cleavage of •trans,trans•, all from divinylcyclobutane. This ratio, k_{VCH}/k_{BD}, then becomes $10^{\Delta A + 4.1/\theta}$, where ΔA must be −0.96 to accommodate the experimental ratio of 4.02 at 575.3°K. Better agreement with the experimental value of ΔA = −0.75 is achieved by this scheme.

Another sighting on the heat of formation of the transition state for the cleavage of the trans,trans diradical to butadiene may be obtained from the thermal decomposition of *trans*-divinylcyclobutane to butadiene: log $k_{BD} = 13.1 - 39.3/\theta$ and ΔH_f°[*trans*-DVCB → DB] = 82.3 kcal/mol. On the assumption that this cleavage cannot be concerted,[2] it may proceed through the intermediacy of the trans,trans diradical.

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(45) It is thinkable that the trans,trans diradical proceeds to *cis*-divinylcyclobutane by way of the transiently intermediate *meso-trans,-trans*-cycloocta-1,5-diene. Beyond recalling that the ΔH_f° of *trans*-cyclooctene is +2.18 kcal/mol or 9.26 kcal/mol greater than the ΔH_f° of *cis*-cyclooctene (−7.08 kcal/mol[22]) and noting that *cis,trans*- or *meso*- and *rac-trans,trans*-cycloocta-1,5-diene would have to possess ~40 kcal/mol more strain than *cis,cis*-cycloocta-1,5-diene before thermodynamics would make their involvement improbable, little can be offered beyond our intention to place at least the cis,trans isomer on the energy surface.

(46) The two experimental points which remain after omission of those at 338.9 and 358.1°, in accord with the authors' own skepticism, and that at 299.5°, in view of the drastic variability of the ratio with time, give the ratio of butadiene to 4-vinylcyclohexene at 327.3° = 0.232 ± 0.012 and at 313.3° = 0.211 ± 0.023. From these two points the activation energy of formation of butadiene is calculated to be 4.8 kcal/mol greater than that of 4-vinylcyclohexene. However, the experimental error may be as much as ±8 kcal/mol. Agreement between the calculated value and this observed value (reversed in Benson's discussion) can scarcely "be taken as a confirmation of our estimates and another measure of the self-consistency of the scheme."[5]

The ratio of 4-vinylcyclohexene to butadiene is then determined by the ratio of the sum of the rates of formation of the cis,trans and cis,cis diradicals to the rate of cleavage of the trans,trans diradical. From the data of Hammond and DeBoer,[18] log $k_{\mathrm{VCH}}/k_{\mathrm{BD}} = (-1.035 \pm 0.45) + (4.45 \pm 0.75)/\theta$. Although coincidence cannot be excluded, the near identity of the expression with that observed in the thermal reaction of cycloocta-1,5-diene $[-0.95 + 4.1/\theta]$ is consistent with the hypothesis above that the product-determining phases of the two thermal reactions are the same. Within the experimental error, these two lines of reasoning predict identical values for the heat of formation of the butadiene-determining transition states ($\Delta H_f°$-[·trans,trans· → BD]). The agreement between 81.1 ± 2.0 kcal/mol from cycloocta-1,5-diene and 82.3 kcal/mol from *trans*-divinylcyclobutane is sufficiently close to warrant retention of the working hypothesis.[47] If $\Delta H_f°$[·trans,trans·] is taken as 66 kcal/mol, it follows that the activation energy for cleavage of the trans,trans diradical is 15 ± 3 kcal/mol and the activation energy for dimerization of butadiene to the trans,trans diradical should be 28.9 ± 2 kcal/mol ($\Delta H_f°$[COD → BD] − $\Delta H_f°$[2BD]).

It is now appropriate to examine the data on the Diels–Alder dimerization of butadiene. Of the three kinetic investigations in the literature,[9] those of Rowley and Steiner [log $k = 11.14 - 26.8/\theta$] (k in cc/(mol sec))[12] and Vaughan [log $k = 10.8 - 26.0/\theta$][10] are concordant with the heats of formation of 2 mol of butadiene [$\Delta H_f° = +52.2$ kcal/mol][8] and 4-vinylcyclohexene [$\Delta H_f° = +17.5$ kcal/mol][14] and the kinetics of the decomposition of 4-vinylcyclohexene to butadiene of Tsang [log $k = 15.20 - 62.0/\theta$].[13] From these values, $\Delta H_f°$[BD → VCH] = 79.2 kcal/mol may be derived in a self-consistent manner (see Figure 6E).[48] This most probable[9] experimental value for the heat of formation of the Diels–Alder transition state is close enough to that of the cleavage of the trans,trans diradical to butadiene ($\Delta H_f°$[·trans,trans· → BD] = 81.1 ± 2.0 or 82.3 kcal/mol) to admit the possibility that this Diels–Alder reaction occurs by the two-step mechanism. It is obviously necessary to assume that the rate (and energy of activation) of dimerization of butadiene to the cis,cis and/or the cis,trans diradical is comparable to the rate of dimerization to the trans,trans diradical and that the formation of ·cis,cis· and ·cis,trans· is followed by rapid and essentially exclusive closure to 4-vinylcyclohexene.

If these assumptions turn out to be incorrect and the true heat of formation of the Diels–Alder transition state is no higher than 79.2 kcal/mol, while the heats of formation of the transition states for the hypothetical formations of the cis,cis and cis,trans diradicals are significantly higher than that of the trans,trans diradical, then the dimerization to 4-vinylcyclohexene proceeds by a concerted mechanism.

Inconclusive though the argument must remain at this moment, it is clear that the magnitude of the concert in this Diels–Alder reaction, if it be not zero, is at best small. Support for this conclusion may be found in the observations that the dimerization of butadiene also leads to cycloocta-1,5-diene[20] and to *trans*-1,2 divinylcyclobutane[17] in small amounts which, however, increase with rising temperature. The crude data on the formation of cycloocta-1,5-diene[20] were never intended to serve as the basis for the calculation of activation parameters, but if the data at 270° are omitted on the grounds that cycloocta-1,5-diene is beginning to rearrange at that temperature, the expression log $[k_{\mathrm{VCH}}/k_{\mathrm{COD}}] = -2.0 + 6.5/\theta$ can be derived. Similarly, the expression, log $[k_{\mathrm{VCH}}/k_{\mathrm{DVCB}}] = -0.4 + 3.5/\theta$, can be calculated from the data available at 25°[49a] and 110°.[49b] It thus appears that two processes, tentatively associated with the hypothetical dimerization of butadiene to ·trans,trans·, are competitive and have activation energies higher than that of the Diels–Alder process by approximately the amount indicated by examination of the reverse cleavage reactions. Only in the event that butadiene should dimerize to the cis,cis and cis,trans diradicals at an appropriately faster rate than it dimerizes to the trans,trans diradical can the Diels–Alder be two step instead of concerted.

We are hopeful that a full study of the dimerization of butadiene coupled with a reinvestigation in the gas phase of the rearrangements of *trans*-1,2-divinylcyclobutane will bring the question of the mechanism of the dimerizations of butadiene closer to a credible solution. Meanwhile, we do not share Benson's conviction that the dimerization to 4-vinylcyclohexene is a two-step process (B of Figure 1),[5] but lean toward the two-stage process (C of Figure 1) of Woodward and Katz,[4] modified to remove the conflict with the dictates of orbital symmetry[2] in which the original formulation now finds itself.

We would prefer to postpone a detailed discussion of this two-stage process until the results of current experiments can be brought to bear. Briefly, however, in this conceptual scheme the basic model for concerted and nonconcerted Diels–Alder reactions, ene reactions, and cycloaddition reactions is taken to be the unassisted, end-to-end dimerization of two double bonds. This step is imagined to generate noninteracting, singlet diradicals in their conformation of lowest energy. In the nonconcerted reactions, corrections on this model may include energy-raising terms (1) for generation of the diradicals in conformations more appropriate to the completion of the reaction, (2) for rotations essential to the reaction, and (3) for any activation energies of rehybridization associated with the cyclization step. Concerted reactions include an energy-lowering correction (4) for overlap in the immediate precursor of the transition state for cyclization. Concertedness or its absence depends on whether correction 4 exceeds correction 1 sufficiently to bring the free energy of activation below that of the nonconcerted reaction or a plausible model thereof.

An illustrative example can be constructed around the closely related but revealingly simpler system of ethylene-butadiene, cyclohexene, and vinylcyclobutane. Comparison with the butadiene–butadiene system serves

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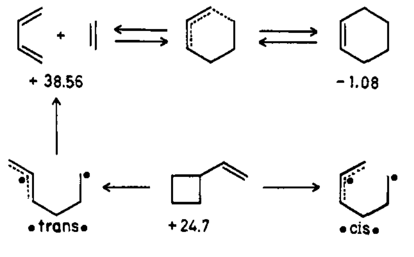
[47] We intend to reexamine the kinetics of the thermal reorganizations of *cis*- and *trans*-1,2-divinylcyclobutane in the gas phase in order to obtain activation parameters which may be confidently compared with those obtained from cycloocta-1,5-diene.

[48] It should be noted that the third investigation of butadiene dimerization gives a considerably lower value [log $k = 9.96 - 23.7/\theta$].[11]

[49] (a) C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, **93**, 4815 (1971). (b) This datum is reported at 110° in the text[17] and at 150° for 18 hr in the Experimental Section. Corrected for decomposition by taking 6% instead of 4–5% and taking 150° as the temperature of reaction leads to log $[k_{\mathrm{VCH}}/k_{\mathrm{DVCB}}] = -0.5 + 3.2/\theta$.

to reveal the origin of the ambiguity of mechanism in the Diels–Alder reaction. The heats of formation of butadiene (+26.11),[8] ethylene (+12.45),[8] and cyclohexene (−1.08)[8] are known while that of vinylcyclobutane (+24.7)[14] is calculated with the usual reservations (*vide supra*). The kinetics of the Diels–Alder reaction of butadiene and ethylene ($\log k = 7.19 - 27.5/\theta$, k in l./(mol sec));[12] $\Delta H_f°[\mathrm{BD/E} \rightarrow \mathrm{CH}] = +66.1$ kcal/mol) and of its reverse, the decomposition of cyclohexene ($\log k = 15.02 - 66.7/\theta$[13] and $\log k = 15.16 - 66.2/\theta$;[50] $\Delta H_f°[\mathrm{CH} \rightarrow \mathrm{BD/E}] = 65.6$ kcal/mol) are known. The kinetics of the decomposition of vinylcyclobutane is unknown, but may be taken as that of isopropenylcyclobutane ($\log k = 14.61 - 51.0/\theta$;[51] $\Delta H_f°[\mathrm{VCB} \rightarrow \mathrm{BD/E;\ CH}] = +75.7$ kcal/mol), which undergoes thermal reorganization to isoprene and ethylene (1.3 parts) and 1-methylcyclohexane (1.0 part). Since the ratio of the two processes is invariant with temperature, the activation energies for the two processes are identical.



If these energy parameters are placed on the energy diagram published by Bartlett,[52] the analysis can be developed. In the previous terms of the more complicated *trans*-1,2-divinylcyclobutane, it may be inferred that here, too, the favored process involves the *trans*-hex-2-en-1,6-diyl diradical (•trans•) and that the formation of cyclohexene involves the *cis*-hex-2-en-1,6-diyl diradical (•cis•). It is reassuring to the previous discussion that there is no significant difference in ease of formation between the two geometrically isomeric diradicals. The heat of formation of •cis• must be calculated since experiments similar to those involving deuterium-labeled, optically active 4-vinylcyclohexene are lacking here. Addition of +82.0 kcal/mol, the strength of a primary–primary bond ($\mathrm{RCH_2{-}CH_2R}$), and subtraction of 14.0 kcal/mol for allylic resonance from the heat of formation of cyclohexene gives $\Delta H_f°[\bullet\mathrm{cis}\bullet] = 67.2$ kcal/mol. Use of Benson's value of 10–12 kcal/mol for allylic resonance would give a slightly higher value. This minimal activation energy for the two-step mechanism is not so much higher than the heat of formation of the transition state for the Diels–Alder reaction to constitute convincing grounds for favoring the concerted mechanism. But when it is recalled that the probable activation energy for cleavage of the trans,trans diradical in the butadiene–butadiene system was 15 ± 3 kcal/mol and that the activation energy for cleavage of the unstabilized tetramethylene diradical is about 7.0 kcal/mol,[53,54] it becomes reasonable to add to the estimated $\Delta H_f°[\bullet\mathrm{cis}\bullet]$ an activation energy for its cleavage. The two-step process for the formation of cyclohexene from butadiene and ethylene then loses its energetic viability.

Experimental Section

Ir were recorded on a Perkin-Elmer Model 421 spectrophotometer and Model 337 grating spectrophotometer. Nmr spectra were obtained on a Varian A-60 spectrometer and are reported in parts per million on the δ scale. Analytical spectra for estimation of deuterium were taken on the Varian Model HA-100 spectrometer. Mass spectra were obtained on a Consolidated 20-103C instrument and on an Allied Electric Industry MS 9 instrument. Melting and boiling points are uncorrected. Rotations were measured with a Rudolph Model 200 photoelectric polarimeter and a Perkin-Elmer 141 polarimeter. Analyses were carried out by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim, Germany.

Resolution of 3-Cyclohexene-1-carboxylic Acid. (a) (*R*)-(+)-3-Cyclohexene-1-carboxylic Acid. Ethyl 3-cyclohexene-1-carboxylate[55] (bp 90° (20 mm), $n^{23}\mathrm{D}$ 1.4548) was saponified to the racemic acid (bp 118° (8 mm), $n^{22}\mathrm{D}$ 1.4804).[56] Although partial resolution and assignment of absolute configuration have been accomplished,[33] resolution is better effected by crystallization of the brucine salt from acetone [124 g of acid, 388 g of brucine, 1980 ml of acetone; seeding; 12-hr standing]. The progress of the resolution is followed by recovery of small quantities of acid which was purified by evaporative distillation prior to polarimetry: (I) 275 g of brucine salt, recrystallized from 1375 ml of acetone; (II) 180 g, 1020 ml, $[\alpha]^{26}\mathrm{D}$ +33.1° (neat, 0.5-dm tube); (III) 124 g, 1100 ml; (IV) 68 g, 800 ml, +53.8°; (V) 26.9 g, 400 ml; (VI) 12.2 g, 113 ml, +58.5°; (VII) 8.2 g, 113 ml, +59.2°; (VIII) 2.83 g, . . . , +58.6°.

The resolved salt (87.0 g) was dissolved in 400 ml of H_2O, acidified cautiously with 22 ml of concentrated HCl, and extracted continuously for 30 hr with 300 ml of ether. The residue from the dried (anhydrous Na_2SO_4) ethereal solution was distilled yielding 19.2 g of (*R*)-(+)-4-carboxycyclohexene, bp 114–115° (7 mm), $[\alpha]^{30}\mathrm{D}$ +119.9°, $[\alpha]^{30}{}_{578}$ +123.5°, $[\alpha]^{30}{}_{546}$ +140.7° (neat, 1-dm tube).

Catalytic hydrogenation (Pt in ethyl acetate) afforded cyclohexanecarboxylic acid, mp 28–29°, $[\alpha]^{27}\mathrm{D}$ 0.0°.

(b) (*s*)-(−)-3-Cyclohexene-1-carboxylic Acid. From the mother liquor from the first crystallization above (272 g in 1375 ml, very slow crystallization), the brucine salt of the enantiomeric acid was obtained: (I) 200 g, 1000 ml, $[\alpha]^{27}{}_{578}$ −36.2° (*c* 1.54, CCl_4) of the recovered acid; (II) 152 g, . . . , −53.8°; (III) 110 g, 775 ml, −69.4°; (IV) 83 g, 650 ml, −82.4°; (V) 50.6 g, 520 ml, −91.7°; (VI) 32.9 g, 350 ml, −101.3°; (VII) 23.7 g, . . . , −108.3°. (This value compares with $[\alpha]^{27}{}_{578}$ +109.9° (*c* 1.01, CCl_4) for the dextrorotatory enantiomer.)

***N*,*N*-Dimethyl-3-cyclohexene-1-acetamide. (a) Arndt–Eistert Synthesis.** Within 15 min 17.38 g (137.8 mmol) of (+)-3-cyclohexene-1-carboxylic acid, $[\alpha]^{30}\mathrm{D}$ +119.9° (neat), was added with stirring to 23.8 g (200 mmol) of freshly distilled thionyl chloride, stirred at room temperature for 18.5 hr, and then refluxed for 2 hr. Distillation yielded a forerun of thionyl chloride and 18.9 g (130.8 mmol, 95%) of (+)-3-cyclohexene-1-carbonyl chloride, bp 82° (20 mm) [lit.[57] 90° (20 mm)], after redistillation, bp 79° (17 mm), $[\alpha]^{28}\mathrm{D}$ +79.8°, $[\alpha]^{28}{}_{578}$ +83.8°, $[\alpha]^{28}{}_{546}$ +94.3°, $[\alpha]^{28}{}_{365}$ +258.5° (*c* 3.32, CCl_4).

A solution of 17.76 g (123.0 mmol) of the above (+)-3-cyclohexene-1-carbonyl chloride in 80 ml of ether was added dropwise with stirring to an ice-cold solution of diazomethane, prepared by adding 26.1 g (300 mmol) of *N*-nitroso-*N*-methylurea in small portions to a stirred mixture of 120 ml of 50% aqueous KOH and 750 ml of ether at 0° and drying the ethereal layer over KOH pellets. After the mixture had reacted overnight, solvent and excess diazomethane were distilled at room temperature under reduced pressure. The residual yellow diazo ketone, without further purification, was dissolved in a mixture of 360 ml of dioxane, 64 ml of H_2O, and 75 g (1.1 mol, 14-fold excess with respect to acid chloride) of liquid dimethylamine. At 0°, 12 ml of 10% aqueous $AgNO_3$, 1.2 g of Ag_2O, and 2.4 ml of CH_3OH were added. Nitrogen evolution started at once. The reaction mixture was allowed to warm to room temperature and was then heated at 55–60° for 1.5 hr, when nitrogen evolution had ceased. The reaction mixture was cooled

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to 0°, slowly acidified to pH ~5 with a mixture of 150 ml of concentrated HCl and 150 ml of H_2O, and then filtered.

Freed of most of the solvent by evaporation, the mixture was extracted thrice with 100 ml of ether. The combined ethereal extracts were washed with 50 ml of water, dried over sodium sulfate, filtered, and concentrated to a residue, vacuum distillation of which yielded 15.82 g (77%) of (+)-*N*,*N*-dimethyl-3-cyclohexene-1-acetamide, bp 86° (0.1 mm); nmr δ 5.60 (broad s, 1.9), 3.00 (s, 3.0), 2.85 (3.0), 2.3–1.2 (complex m, 9.1); ir (cm^{-1}) 3010 m (cis disubstituted alkene), 2910 m, 2825 w, 1655 s (carbonyl, tertiary amide), 1495 w, 1460 w, 1440 m, 1400 m, 1270 m, 1190 w, 1135 m, 1045 w, 1055 w, 960 w, 915 w, 870 w, 655 m-s (cis disubstituted alkene), 605 w; $[\alpha]^{28}_{\mathrm{D}}$ +62.2°, $[\alpha]^{28}_{578}$ +63.0°, $[\alpha]^{28}_{546}$ +71.7°, $[\alpha]^{28}_{365}$ +192.5° (*c* 1.87, CCl_4).

Repetition of the sequence reported by Klein[57] afforded methyl 3-cyclohexene-1-acetate [75% based on 3-cyclohexene-1-carboxylic acid of $[\alpha]^{26}_{\mathrm{D}}$ +46.2° (neat, 1 dm)], bp 72–75° (7 mm), $[\alpha]^{26}_{\mathrm{D}}$ +28.3° (neat, 1 dm), by way of 3-cyclohexene-1-carbonyl chloride [bp 71° (9 mm); $[\alpha]^{27}_{\mathrm{D}}$ +34.6° (neat, 1 dm)]. Saponification of the methyl ester afforded 3-cyclohexene-1-acetic acid (94%), bp 92–94° (0.3 mm); $[\alpha]^{27}_{\mathrm{D}}$ +30.8° (neat, 1 dm).

In attempts to resolve 3-cyclohexene-1-acetic acid, crystalline salts were obtained from the partially resolved acid $[\alpha]^{27}_{\mathrm{D}}$ +30.8° (neat, 1 dm), in the manner described, reconverted to acid, the change in rotation of which is reported. Ephedrine hydrate (1.3 g) and 1 g of acid in 1 ml of 95% ethanol afforded 0.37 g of salt: mp 91–93°; recovered acid showed $[\alpha]^{26}_{\mathrm{D}}$ 39.2° (neat, 1 dm). Cinchonidine (1.18 g) and 1 g of acid in 1.5 ml of benzene gave 0.38 g of salt: mp 112–124° dec; recovered acid, $[\alpha]^{26}_{\mathrm{D}}$ +26.8° (neat, 1 dm). Quinine (0.867 g) and 0.75 g of acid in 1.4 ml of acetone afforded 0.80 g of salt: mp 126–128° dec; recovered acid, $[\alpha]^{26}_{\mathrm{D}}$ +28.8° (neat, 1 dm).

A mixture of 6.72 g (48.0 mmol) of partially active (+)-3-cyclohexene-1-acetic acid, $[\alpha]^{26}_{\mathrm{D}}$ +29.9° (*c* 1.79, CCl_4), and 8.25 g (70 mmol) of freshly distilled thionyl chloride afforded 6.57 g (41.5 mmol) of colorless (+)-3-cyclohexene-1-acetyl chloride: bp 95–96° (20 mm); $[\alpha]^{23.5}_{\mathrm{D}}$ +27.4° (*c* 1.71, CCl_4).

Following the procedure of Gilbert,[58] to a solution of 6.75 g (150 mmol) of anhydrous dimethylamine in 20 ml of sodium-dried benzene, a solution of 6.57 g (41.5 mmol) of the above sample of (+)-3-cyclohexene-1-acetyl chloride in 20 ml of dry benzene was added slowly at 0° with stirring. Stirring continued for 21 hr at room temperature. After distillation, 5.60 g (33.5 mmol) of (+)-*N*,*N*-dimethyl-3-cyclohexene-1-acetamide was obtained, bp 85–87° (0.15 mm), $[\alpha]^{25}_{\mathrm{D}}$ +25.0° (*c* 1.49, CCl_4).

(b) **By Grignard Extension.** (+)-3-Cyclohexene-1-carboxylic acid, $[\alpha]^{26}_{\mathrm{D}}$ +101.2° (neat, 1 dm), was reduced with $LiAlH_4$ in ether to (+)-4-cyclohexenylmethanol, $[\alpha]^{27}_{\mathrm{D}}$ +89.2° (neat, 1 dm), which had the same ir and nmr spectrum as a sample prepared from 3-cyclohexene-1-carboxaldehyde by $LiAlH_4$ reduction.[59] A sample of racemic alcohol was converted to 4-chloromethylcyclohexene by treatment with thionyl chloride, bp 73° (29 mm); n^{23}_{D} 1.4825. Carbonation of the Grignard reagent of this chloride with Dry Ice in ether afforded 3-cyclohexene-1-acetic acid: bp 94–96° (0.06 mm) [lit.[60] 93–95° (0.05 mm)]; ir and nmr identical with the sample prepared by the Arndt–Eistert synthesis above. Treatment of the acid with thionyl chloride afforded the acid chloride which was treated with dimethylamine to give *N*,*N*-dimethyl-3-cyclohexene-1-acetamide: ir and nmr spectra identical with those of the sample prepared above.

Optically Active and Deuterated 4-Vinylcyclohexene. (a) By the Wittig Olefin Synthesis. Following the method of Wiley, *et al.*,[61] 39.4 g (0.15 mol) of triphenylphosphine in 95 ml of dimethylformamide was treated dropwise with stirring with 22.2 g (0.14 mol) of bromine at ≦50°. To the resulting thick slurry, 15.7 g (0.14 mol) of 3-cyclohexene-1-methanol, $[\alpha]^{27}_{\mathrm{D}}$ +89.2° (neat, 1 dm), was added dropwise at ≦50°. The flask having been fitted for vacuum distillation, all material boiling up to 90° (6 mm) was removed, collected in a receiver at −70°, poured into 500 ml of H_2O, and allowed to stand 12 hr. The lower layer was separated, dried over anhydrous $MgSO_4$, and distilled to give 4-bromomethylcyclohexene: 17.6 g (72%); bp 56–58 (5.5 mm); n^{25}_{D} 1.5099 [lit.[62] bp 37° (2 mm), n^{25}_{D} 1.5105]; $[\alpha]^{28}_{\mathrm{D}}$ +82.2° (neat, 1 dm).

This bromide (17.8 g, 0.102 mol), 26.6 g (0.102 mol) of triphenylphosphine, and 18 ml of toluene were heated 4.5 days at 115° under N_2. The cooled solid was triturated with ether to give 30 g of crude material (dec pt 207–211°): $[\alpha]^{28}_{\mathrm{D}}$ +7.8° (*c* 0.0512, $CHCl_3$, 0.5 dm). The phosphonium bromide was converted to 4-vinylcyclohexene by treatment of its corresponding ylide with formaldehyde according to the procedure of Hauser, *et al.*[63] Purification was effected on a 6 m × 0.5 in. column of 20% Carbowax 4000 on 110–120 mesh Anakrom ABS at 110°: $[\alpha]^{26}_{\mathrm{D}}$ +77.1° (neat, 1 dm), $[\alpha]^{25}_{\mathrm{D}}$ +115 ± 1° (*c* 0.21–1.03, CCl_4).

In an attempt to prepare 2,2-dideuterio-1-(3-cyclohexenyl)ethene, triphenylmethyl-d_3-phosphonium bromide, prepared by base-catalyzed exchange of triphenylmethylphosphonium bromide in D_2O by the procedure of Doering and Gilbert,[7] was converted to the ylide by treatment with *n*-butyllithium in ether which was then allowed to react with 3-cyclohexene-1-carboxaldehyde following the procedure for methylenecyclohexane.[64] The resulting 4-vinylcyclohexene, purified by glpc (4 m × 0.5 in. column, 15% diethylene glycol succinate on 40–60 mesh Kieselguhr), showed protons in the region of vinylic methylene absorption in the nmr and revealed peaks in the mass spectrum corresponding to d_3 as well as to d_2.

(b) **By Cope Elimination.** To a 250-ml, three-necked flask equipped with drying tube, addition funnel, N_2 inlet, and magnetic stirring bar which had been dried by heating under continuous flushing with dry N_2, there was added 1.26 g (33.2 mmol) of $LiAlH_4$ in 80 ml of anhydrous ether. Over a period of 1.5 hr, 10.0 g (59.8 mmol) of *N*,*N*-dimethyl-3-cyclohexene-1-acetamide in 50 ml of ether was added dropwise with stirring at 0°. After the addition, the reaction mixture was stirred at room temperature for 45 min, refluxed for 20.5 hr, and then treated dropwise with H_2O at 0° until all the aluminum oxide had precipitated. The ethereal solution was filtered and the aluminum oxide thoroughly washed with 130 ml of ether in three portions. The combined ethereal solutions were dried over solid KOH and concentrated to a residue which was distilled under reduced pressure to yield 6.44 g (42.2 mmol) of 2-(3-cyclohexen-1-yl)ethyldimethylamine: bp 83.5–85.0° (14 mm); nmr δ 5.58 (d, 2, J = 2 Hz), 2.11 (s, 6), 2.50–1.20 (complex m, 11); ir (cm^{-1}) 3010 m (cis disubstituted alkene), 2905 m, 1840 m, 1750 m, 1655 w (C=C), 1555 w, 1470 m, 1345 w, 1270 w, 1170 w, 1140 w, 1095 w, 1040 m (tertiary amine), 1010 w, 920 w, 905 w, 870 w, 850 w, 655 m-s (cis disubstituted alkene).

Anal. Calcd for $C_{10}H_{19}N$: C, 78.4; H, 12.5; N, 9.1. Found: C, 78.9; H, 11.7; N, 9.2.

The same procedure was applied to 15.0 g of (+)-*N*,*N*-dimethyl-3-cyclohexene-1-acetamide, $[\alpha]^{28}_{\mathrm{D}}$ +62.2° (*c* 1.87, CCl_4), in 120 ml of dry ether and 2.25 g of lithium aluminum deuteride (Merck Sharp and Dohme) in 50 ml of dry ether to yield 10.65 g of (+)-2-(3-cyclohexen-1-yl)-*1*,*1*-d_2-ethyldimethylamine: bp 89° (16 mm); $[\alpha]^{27}_{\mathrm{D}}$ +78.8°, $[\alpha]^{27}_{578}$ +82.2°, $[\alpha]^{27}_{546}$ +93.7°, $[\alpha]^{27}_{365}$ +242° (*c* 1.81, CCl_4); nmr vinylic to all other hydrogen, 2.0 to 15.1.

Racemic undeuterated, racemic deuterated, and optically active deuterated samples of 2-(3-cyclohexen-1-yl)ethylamine were oxidized with hydrogen peroxide to the corresponding amine oxides and heated to yield racemic, racemic deuterated, and partially and completely resolved deuterated 4-vinylcyclohexene, following an adaption of the procedure described by Gilbert.[7,58] At room temperature 4.0 g of 30% aqueous H_2O_2 was added to 4.0 g of 2-(3-cyclohexen-1-yl)ethyldimethylamine in 10 ml of CH_3OH. After being stirred for 38 hr at ambient temperature, the reaction mixture was treated with a small quantity of 1% platinum on charcoal to decompose the excess H_2O_2. The amine oxide solution was filtered and concentrated under reduced pressure. After removal of the solvents, the heating bath was slowly raised to 120–130°. The products of pyrolysis distilled at about 30 mm and were collected in a trap cooled with Dry Ice. Two 10-ml portions were extracted with *n*-pentane, washed twice with 3 ml of H_2O, dried over an-anhydrous $MgSO_4$, filtered, and concentrated to a residue, distillation of which afforded 1.91 g (17.7 mmol) of 4-vinylcyclohexene: bp 75° (120 mm); glpc on column A (2 m × 0.25 in. 50–60 mesh Anakrom ABS containing 20% di-*n*-decyl phthalate; n = 1210[65]) revealed 4% of *n*-pentane as impurity.

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From 4.5 g (29.0 mmol) of (+)-2-(3-cyclohexen-1-yl)-*1,1-d_2*-ethyldimethylamine, $[\alpha]^{27}D$ +30.2° (*c* 1.12, CCl_4), 1.595 g (14.5 mmol) of (+)-4-vinylcyclohexene-*2,2-d_2*, bp 78–79° (130 mm), was obtained. Purification on column A afforded 1.097 g of product (≥99.8%); $[\alpha]^{29}D$ +43.1°, $[\alpha]^{29}{}_{578}$ +44.5°, $[\alpha]^{29}{}_{546}$ +50.4°, $[\alpha]^{29}{}_{365}$ +134.4° (*c* 1.224, CCl_4); ir (cm^{-1}) 3025 s, 2985 w, 2920 s, 2830 s, 2650 w, 2310 m, 2210 m, 1650 m, 1600 m, 1455 m, 1440 m, 1138 m, 1040 m, 955 m, 935 m, 910 m, 728 s, 715 s, 655 s, 555 w; nmr δ 5.70 (m, 3), 2.20–1.20 (complex m, 7), no end-vinyl hydrogen signals were detectable; mass spectrum 6.3% d_0, 5.0% d_1, 88.8% d_2, no d_3 or d_4 products.

Five determinations of the rotations of (+)-4-vinylcyclohexene-*2.2-d_2* in the concentration range 0.923–1.391 in CCl_4 gave the following results: $[\alpha]^{24}D$ +110.47 ± 0.18°, $[\alpha]^{24}{}_{578}$ +115.93 ± 0.13°, $[\alpha]^{24}{}_{546}$ +131.28 ± 0.19°, $[\alpha]^{24}{}_{365}$ +347.98 ± 0.52°.

To determine deuterium content, three spectra with ten integrations each were recorded on a Varian HA-100 spectrometer operated in the field sweep mode: 1.920 ± 0.004 mol of deuterium per mol of (+)-4-vinylcyclohexene in the end-vinyl position. The mass spectrum revealed 3.9% d_0, 6.2% d_1, 89.9% d_2, and no d_3 or d_4 products.

Deuterium Rearrangement and Racemization of (*R*)-(+)-1,1-Dideuterio-2-(cyclohex-3-enyl)ethene. Apparatus for Thermal Reactions. The thermolysis apparatus consisted of a 12-l. Pyrex vessel, which was located in a well-insulated air thermostat modeled after that of Clark[66] and attached to a vacuum line. Temperature control was established by a Stabiline voltage regulator (Superior Electric Co., Bristol, Conn.) and a Thermotrol temperature controller, Model 1053 A (Hallikainen Instruments, Richmond, Calif.). The Thermotrol unit applied a negative feedback signal during "proportional operation" to produce an "on" period which was a function of the bridge unbalance voltage. Temperatures were measured with an iron–constantan thermocouple and a millivolt potentiometer, No. 8686 (Leeds and Northrup Co., Philadelphia, Pa.). The temperature gradient over the vessel was found to be ±0.2° and the change of temperature over extended periods of time at one spot was ±0.02°. We are indebted to Dr. Beasley for the construction of this apparatus.[67]

Preliminary Kinetic Runs. Preliminary experiments were performed with 40–45 mg of racemic or deuterated, partially optically active 4-vinylcyclohexene. The partial pressure of starting material in the 12-l. vessel at 360° was in the range of 1.2–1.4 mm. For such a complex molecule as 4-vinylcyclohexene this pressure range should be well above the pressure sensitive region of rate constants.

To check the transfer technique starting material was degassed before being transferred into the vessel at 360° and recovered after 16 min. Vpc analysis on column A (80°, 60 cc He/min) with methylcyclohexane as internal standard gave 99.1 ± 0.9% recovery.

After 30 hr at 360° a product was obtained which showed at least 17 peaks on column A, of which that with the retention time of 4-vinylcyclohexene (11 min) amounted to 27% of starting material. Seasoning of the vessel with 4-vinylcyclohexene or adding aniline or diphenylamine did not measurably affect the recovery of the starting material or the number of products. A shorter run for 15 hr at 360° led to recovery of starting material in 55% of theory (column A). The ir of 4-vinylcyclohexene recovered by vpc was consistent with that of starting material except for one minor absorption. Further purification of recovered material on column B [4 m, 10% silver tetrafluoroborate and 20% Carbowax 600 on Chromosorb P (acid washed) 60–80 mesh; *n* = 3600[65]] (65°, 90 cc He/min) revealed that the 4-vinylcyclohexene (retention time 55 min) had been contaminated with two impurities of shorter retention times (30 and 50 min, respectively). 4-Vinylcyclohexene recovered from this second vpc separation had an ir spectrum identical in all respects with that of starting material.

A run with partially optically active material, $[\alpha]^{29}D$ +43.1° (*c* 1.224, CCl_4), at 360° for 15 hr resulted in a product of which recovered starting material, after purification on columns A and B, had a rotation of $[\alpha]^{27}D$ +24.6° (*c* 0.456, CCl_4), the equivalent of 43% racemization. Integration of the nmr spectrum of this material established an increase in end-vinyl hydrogen corresponding to a nearly equilibrium distribution of deuterium between the end-vinyl and allylic position and showed the deuterium rearrangement to be faster than the racemization.

Final Kinetic Runs. The racemization and the deuterium rearrangement of (*R*)-(+)-1,1-dideuterio-2-(cyclohex-3-enyl)ethene could be studied simultaneously by following the loss of optical activity and the decrease in deuterium content in the end-vinyl position, owing to the relatively small difference in reaction rates of these two processes. The thermal isomerizations were studied in the gas phase at about 1.25 mm at five temperatures between 335 to 380°. Loss of optical activity was followed up to about 30% conversion. Individual rotations were measured in CCl_4 and are the average of at least three measurements.

Reaction times, temperatures, and specific rotations at four wavelengths of recovered starting material which had been purified by preparative vpc on columns A and B (conditions as previously described) are given in Table IV[68] for all individual runs. In addition, the calculated initial pressures, temperatures, and deuterium content in the end-vinyl position are recorded. The amount of deuterium was calculated from two or three individual sets of ten integrals for each run. Errors indicate the mean errors of the average of these integrals.

In run no. 87 a tenfold molar excess of aniline was added to check for radical chain processes. No difference in rotation and deuterium rearrangement exceeding experimental error was found.

The amount of 4-vinylcyclohexene produced by decomposition of starting material and redimerization of the resultant 1,3-butadiene was calculated for the most severe run; 3 hr at 380°. To check this calculation experimentally 6.38 mg (0.118 mmol) of 1,3-butadiene (Union Carbide, >99% purity) was heated for 3 hr at 380°, and the amount of 4-vinylcyclohexene formed was analyzed by vpc on column C (6 m, 20% Silicone SE 30 on Chromosorb P 60–80 mesh) at 118° and 65 cc of He/min with methylcyclohexane as internal standard. Only 1.5% of the 1,3-butadiene had dimerized to 4-vinylcyclohexene.

Intramolecularity of the deuterium rearrangement was established by a mass spectrometrical comparison of the deuterium contents of the starting material and of the product of the longest run at the highest temperature (no. 98). Within experimental error both samples contained the same amount of deuterium: starting material, 1.86 atoms of D/mol, and product, 1.91 atoms of D/mol. No indication of tri- or tetradeuteriated material was found in either case.

The possibility of nonlinearity of rotation was checked by preparing known mixtures of 34.6, 56.6, and 84.5% of optical purity. These were found to be within 0.8% of the true value in each case.

Calculations of Rate Constants and Activation Parameters. Rate constants for the racemization were calculated by the first-order equation $k = (2.303/t) \log (\alpha_0/\alpha)$ where α_0 denotes the initial rotation and α the rotation at time *t*. Those constants calculated for the rotations at λ 365 nm are given in Table IV.[68] The rearrangement of deuterium was assumed to be an opposing first-order reaction. With the assumption that the rate constants for the foreward and backward reaction are equal rate constants were calculated according to the equation $k = -(1/2t) \ln [(2A/A_0) - 1]$ where A_0 is the amount of deuterium in the end-vinyl position of the starting material and A the deuterium content at the same position at time *t*. These rate constants are given in Table IV[68] in the microfilm edition. In this calculation any secondary isotope effect is neglected.

Table I gives the average and weighted rate constants for both reactions at the various temperatures and the Arrhenius activation parameters determined by the method of least squares.

Thermal Reaction of Cycloocta-1,5-diene. Cycloocta-1,5-diene (Aldrich) and *o*-xylene (Eastman) were purified by preparative vpc on a 4 m 3/8 in. column of Carbowax 20 M (25%) on Chromosorb A 60–80 mesh. Other materials were either pure enough as obtained or were similarly purified (vinylcyclohexene, Aldrich).

Analysis of the thermal reactions was effected on a 5 m 0.25 in. column of Silicone SE 30 (20%) on Chromosorb P 60–80 mesh, previously washed with NaOH in CH_3OH. It was operated at 26 lb of He with the injector at 172° and the detector at 210°, and the column at 42° (cooling by compressed air) for butadiene and 136° for all the other components. The apparatus was an Aero-

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(68) Tables IV and V will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-3833. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

graph Model 90 P gas chromatograph with a Disc chart integrator Model 207.

A weighed amount of *o*-xylene was used as the internal standard; at the end of each run some benzene was added to minimize loss of the volatile butadiene. Aniline was introduced routinely as an inhibitor of radical reactions. At 42°, the retention time of butadiene was 6.15 min while those of the other substances at 136° were 15.5 (benzene), 27.0 (4-vinylcyclohexene), 32.0 (*o*-xylene), 37.0 (cycloocta-1,5-diene), and 41.0 min (aniline).

Gas chromatographic correction factors relative to *o*-xylene were determined by analysis of known mixtures prepared by weight with the exception of butadiene (vacuum system by pressure and volume). Multiplication of the ratio of the integrated peak of material to that of *o*-xylene by the correction factor gives the true weight of material. Correction factors are as follows: cycloocta-1,5-diene, 1.04 ± 0.007; 4-vinylcyclohexene, 1.02 ± 0.008; butadiene, 1.44 ± 0.02.

In preliminary experiments it was found that good material balances and good first-order plots were obtained in the 12-l. Pyrex flask at the highest temperatures provided a tenfold molar excess of aniline was incorporated as an inhibitor. The rate constants at 359.70 and 330.17° were 410.8×10^{-5} and 55.6×10^{-5} sec^{-1}, respectively, whence $\log k_a = 15.40 - 51.6/\theta$ where $\theta = (2.303)\cdot(1.987)(0.001)T$. The ratios of 4-vinylcyclohexene to butadiene were constant for the different runs at the same temperature but varied from 2.92 at 359.70° to 3.57 at 330.17°, corresponding to a greater activation energy for the formation of butadiene of 5 kcal/mol.

The final study of the kinetics was performed without aniline in a 3.5-l. hand-blown flask of lead–potash glass. Mass balance was good at all conversions up to the highest temperatures and strictly first-order plots were obtained. Individual rate constants were calculated by the method of least squares giving weight to individual points in proportion to the extent of reaction. The experimental data are given in Table V[68] in the microfilm edition. The calculated rate constants and activation parameters, calculated by the method of least squares, have been given in Table II.

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Cyclohexadienyl Cations. III. Kinetics and Mechanism of the Dienone–Phenol Rearrangement in Concentrated Aqueous Acids[1,2]

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Abstract: Rates of the acid-catalyzed rearrangement of 4,4-dimethylcyclohexadienone (**1**) to 3,4-dimethylphenol in aqueous sulfuric acid (35.5–94.7%) and aqueous perchloric acid (37.9–71.0%) have been measured. 3-Deuterio-4,4-dimethylcyclohexadienone has been prepared and was shown to undergo the dienone–phenol rearrangement faster than **1** in both 97.3 and 55.2% sulfuric acid. These results coupled with earlier published information support a mechanism which involves (a) reversible protonation of **1** to produce a hydroxycyclohexadienyl cation followed by (b) rate-determining methyl migration from C-4 to C-3 and finally (c) rapid loss of a proton from C-3 to produce the aromatic product. In addition, our analysis of the acidity dependence of the dienone–phenol rearrangement in sulfuric and perchloric acids suggests that the transition state is less solvated than the ground state. Activation parameters for the isomerization of **1** in 97.2% sulfuric acid have been determined and are discussed.

The application of acidity function theory to the solution of mechanistic problems in organic chemistry has been and continues to be a challenging problem. Some of the recent work in this area has involved a search for more meaningful parameters associated with the kinetic acidity dependence of acid-catalyzed reactions with a view toward expanding the scope and usefulness of Hammett's original work.[3-5] On the other hand, Kresge, *et al.*, have suggested that detailed structural information concerning the transition state can be obtained from a comparison of the acidity dependence of kinetic and equilibrium protonation reactions for certain acid-catalyzed reactions.[6,7] Very recently in a series of very significant papers it was concluded that the number of water molecules required to form the activated complex in ester[8,9] and amide[10] hydrolysis could be determined from the dependence of the hydrolysis rate on acid concentration and water activity provided that the concentration of protonated ester or amide could be measured or estimated as a function of acid concentration. We were interested in ob-

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(1) For paper II in this series, see: V. P. Vitullo, *J. Org. Chem.*, **35**, 3976 (1970).

(2) Supported in part by Grant No. GP-29738X from the National Science Foundation.

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