

# Kinetics of the Unimolecular Isomerization of 1,4-Dichlorobicyclo[2.2.0]hexane in the Gas and Liquid Phase. Radical Stabilization Energy of an $\alpha$ -Chlorine Atom

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**Abstract:** The gas-phase isomerization of 1,4-dichlorobicyclo[2.2.0]hexane to 2,5-dichlorohexa-1,5-diene has been studied in a static system over the temperature range 135–196°. The variation of the total pressure from 0.8 to 300 Torr and an increase in the surface to volume ratio of the reaction vessel had no effect on the rate of isomerization. The Arrhenius equation derived from the rate constants over this temperature range is  $\log k \text{ (sec}^{-1}\text{)} = (13.3 \pm 0.1) - (33.93 \pm 0.16)/\theta$ , where  $\theta = 2.303RT \text{ kcal/mol}$ . These Arrhenius parameters are in good agreement with transition state estimates for a mechanism involving the intermediate formation of a cyclohexane 1,4-diradical. From the activation energy, the radical stabilization energy of an  $\alpha$ -chlorine atom is shown to be  $1.5 \pm 1.0 \text{ kcal/mol}$ . Rates were also measured in the liquid phase at 155 and 175°. In dimethyl sulfoxide as solvent, the isomerization was 10% faster than in the gas phase, whereas in diphenyl ether, there was a 60% increase in rate compared to the gas phase.

The thermal isomerization of bicyclo[2.2.0]hexanes to hexa-1,5-dienes is a bicyclic analog of the well-documented isomerization of cyclobutanes to ethylene.<sup>1</sup> In the compilation by Benson and O'Neal,<sup>1</sup> the opening of the cyclobutane ring is considered to occur *via* a tetramethylene biradical. The effect of a number of ring substituents on the Arrhenius parameters is shown to be consistent with radical stabilization energies obtained by other techniques. Having established a biradical mechanism, the thermal isomerization of cyclobutanes may yield the stabilization energy of substituent groups which have only been studied quantitatively in the cyclobutane system.

However, the isomerization of cyclobutanes requires only electronic reorganization, and a concerted mechanism is possible. Woodward and Hoffmann<sup>2</sup> have shown that the symmetry-allowed process requires distortion of the transition complex and specific steric orientation in the products. In experiments designed to test this stereospecificity, Cocks, Frey, and Stevens<sup>3</sup> found that the isomerization of 6,7-dimethylbicyclo[3.2.0]heptane was completely biradical, although the results of Baldwin and Ford<sup>4</sup> for the isomerization of 7,8-*cis,exo*-dideuteriobicyclo[4.2.0]octane suggested that approximately 30% of the decomposition was occurring *via* a concerted mechanism. Considered together, these results imply that both pathways are feasible for cyclobutane itself, although any substituent which stabilizes the biradical will ensure that isomerization is almost exclusively *via* the biradical mechanism.

Very little quantitative data has been reported for the thermal isomerization of bicyclo[2.2.0]hexanes. The Arrhenius parameters for the parent hydrocarbon<sup>5</sup> are

(1) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS-NBS 21, National Bureau of Standard Reference Data System, U. S. Department of Commerce, Washington, D. C., 1970.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *J. Chem. Soc. D*, 458 (1969).

(4) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

consistent with a biradical mechanism. Attempts to find evidence for a concerted mechanism in the thermal isomerization of some 2,3-disubstituted bicyclo[2.2.0]hexanes were inconclusive.<sup>6</sup> In a recent communication,<sup>7</sup> we have investigated the kinetics of isomerization of a series of 1,4-disubstituted bicyclo[2.2.0]hexanes to 1,5-hexadienes and obtained strong evidence for a diradical intermediate. 1-Chloro-,<sup>8</sup> 1-chloro-4-carbomethoxy-,<sup>9</sup> and 1,4-dicarbomethoxybicyclo[2.2.0]hexane<sup>10</sup> have also been shown to isomerize to 1,5-hexadienes, but apart from the dimethyl ester,<sup>10</sup> no kinetic details have been reported. Considering the limited thermochemical information which is at present available for the range of substituents studied, the results overall are consistent with a biradical mechanism. However, there is no conclusive evidence to rule out a concerted mechanism, although this is unlikely due to steric strain in the bicyclic transition complex<sup>6,7</sup> imposed by the orbital symmetry requirements.<sup>2</sup>

In this and subsequent papers we present detailed kinetics for the thermal isomerization of appropriately substituted 1,4-bicyclo[2.2.0]hexanes in both liquid and gas phases. Solvent effects are generally considered to be small in extrapolating from the nonpolar liquid phases to the gas phase. From the present work, the generality of this hypothesis may be tested.

## Experimental Section

**Preparation of 1,4-Dichlorobicyclo[2.2.0]hexane.** This was prepared from 4-chlorobicyclo[2.2.0]hexane-1-carboxylic acid<sup>11</sup> by the method of Kochi.<sup>12</sup> Lead tetraacetate (8.25 g, 18.7 mmol) and acetic acid (2.0 g, 33.3 mmol) were added to a stirred solution of 4-

(5) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

(6) L. A. Paquette and J. A. Schwartz, *ibid.*, **92**, 3215 (1970).

(7) E. N. Cain, *Tetrahedron Lett.*, 1865 (1971).

(8) R. Srinivasan, *ibid.*, 603 (1967).

(9) K. V. Scherer, Jr., *ibid.*, 5685 (1966).

(10) D. C. Owsley and J. J. Bloomfield, *J. Amer. Chem. Soc.*, **93**, 782 (1971).

(11) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, *ibid.*, **90**, 1014 (1968).

(12) J. K. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

chlorobicyclo[2.2.0]hexane-1-carboxylic acid (3.00 g, 18.7 mmol) in dry benzene (125 ml) under nitrogen. After bubbling nitrogen through the stirred solution for 30 min, dry finely ground lithium chloride (0.825 g, 19.5 mmol) was added in one portion from an attached flask under nitrogen. The solution was then heated to reflux while stirring vigorously and carbon dioxide (73% of theoretical as measured by absorption on "soda asbestos") was evolved over a period of approximately 1 hr. The cooled solution was washed with 15% aqueous perchloric acid (150 ml), water (200 ml), saturated sodium bicarbonate solution (two 200-ml aliquots), 2 *N* sulfuric acid (200 ml), water (200 ml), and saturated brine solution (200 ml), and finally dried over anhydrous sodium sulfate. The benzene was removed by distillation at atmospheric pressure and the residue was sublimed onto a cold finger (at  $-80^{\circ}$ ) at  $45-50^{\circ}$  (0.01 mm) to give 1,4-dichlorobicyclo[2.2.0]hexane as white crystals (480 mg, 17%): mp  $57-58^{\circ}$ ; ir (Nujol) 840, 920, 945, 1040, 1130, 1200, 1240, 1260  $\text{cm}^{-1}$ ; nmr ( $\text{CCl}_4$ ) singlet at  $\tau$  7.4; measured mass 150.000309 (theory 150.000303), 151.996982 (theory 151.997353). *Anal.* Calcd for  $\text{C}_6\text{H}_8\text{Cl}_2$ : C, 47.7; H, 5.3. Found: C, 47.6; H, 5.3.

**Apparatus.** A conventional high-vacuum static system was used for the gas-phase studies. The 1,4-dichlorobicyclo[2.2.0]hexane and the reaction product were confined to a heated section of the inlet manifold constructed exclusively of greaseless stopcocks with Teflon "O" rings. Runs were carried out in a 700-ml cylindrical Pyrex reaction vessel, thermostated in air heated by an aluminum block. The temperature of the thermostat was maintained at  $\pm 0.5^{\circ}$  by an AEI RT2 temperature controller with a platinum resistance thermometer as sensor. Temperatures were measured with a Pt|13% Ph-Pt thermocouple, standardized against a similar thermocouple calibrated by the CSIRO Natural Standards Laboratory, Sydney University. A second reaction vessel of the same dimensions, but packed with pieces of glass tubing so that the surface to volume ratio increased by eightfold, was used for some runs. Both vessels were conditioned by the di-*tert*-butyl peroxide initiated polymerization of 120 Torr of  $\text{C}_2\text{F}_4$  at  $160^{\circ}$ . This process has been shown to be more efficient<sup>13</sup> than the usual pyrolytic carbon coating and kinetic results were reproducible from the initial run.

The liquid-phase studies were carried out in standard nmr tubes. The temperature of the reaction mixture was controlled by suspending the tubes in a refluxing liquid thermostat (1-hexanol at  $154.7 \pm 0.1^{\circ}$  and *p*-cymene at  $174.9 \pm 0.1^{\circ}$  for the present work). The temperature of the refluxing liquid was measured with a mercury in glass thermometer calibrated against a standard platinum resistance thermometer.<sup>14</sup>

**Procedure.** Prior to a run in the gas phase, the vacuum system and reaction vessel were evacuated to less than  $10^{-4}$  Torr. The desired pressure of 1,4-dichlorobicyclo[2.2.0]hexane was sublimed from the sample vessel (heated by a water bath) into the reaction vessel *via* the heated inlet manifold. After the required pyrolysis time, the reaction mixture was shared with a heated gas pipet, which had been previously evacuated. The total pressure in the gas pipet was increased to *ca.* 100 Torr by the addition of nitrogen and the sample introduced into a gas chromatograph *via* a heated greaseless gas sampling valve. The reactant and product were well separated on a 12 ft  $\times$  0.25 in. column packed with 100-120 mesh Celite coated with 5% silicone oil DC 550 and 0.3% Tween. Signals from the flame ionization detector were integrated using a ball and disc integrator. All analyses were performed in duplicate.

Samples for liquid-phase study were prepared by dissolving 1,4-dichlorobicyclo[2.2.0]hexane (*ca.* 15%) in dimethyl-*d*<sub>6</sub> sulfoxide or diphenyl ether in an nmr tube with a small amount of decalin (*ca.* 15 mg) as an internal standard. The solutions were degassed by repeated application of the freeze-thaw technique and sealed under vacuum. Prior to a run, the tubes were preheated in an oven at *ca.*  $50^{\circ}$  below the reaction temperature. They were then immersed in the refluxing liquid thermostat for the desired reaction time, upon which the reaction was quenched by immersing the tubes in cold water. The mixture was analyzed by integration (mean of three runs) of the  $^1\text{H}$  nmr absorptions in the olefinic and aliphatic regions of the spectrum. These integral areas are related by

$$\frac{\text{olefinic integration}}{\text{aliphatic integration}} = \frac{4x}{800 - 4x}$$

where  $x$  = per cent diene. Integration against decalin provided an

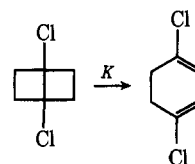
(13) R. K. Solly and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 427 (1969).

(14) Kindly loaned by the Diffusion Research Unit, Australian National University.

independent check on all calculations and a proton mass balance. In the case of dimethyl-*d*<sub>6</sub> sulfoxide, a small correction for the interference due to nondeuterated solvent was made by comparing the aliphatic signal area at 0 and 100% reaction.

## Results

In both gas and liquid phases the thermal isomerization of 1,4-dichlorobicyclo[2.2.0]hexane was shown to yield only one product by  $^1\text{H}$  nmr analysis and gas chromatography with both polar (triscyanoethoxypropane) and nonpolar (silicone oil DC 550) stationary phases. The final product was isolated by preparative gas chromatography and the ir and  $^1\text{H}$  nmr spectra found to be identical with literature values for 1,4-dichlorohexa-1,5-diene.<sup>15</sup>



Plots of the logarithm of per cent undecomposed reactant against time for at least six different times were linear to more than 90% decomposition. Rate constants obtained graphically from these plots are shown in Table I.

**Table I.** Rate Constants for the Isomerization of 1,4-Dichlorobicyclo[2.2.0]hexane

Temp, $^{\circ}\text{C}$	134.8	147.5	154.7	154.7	154.7
$k \times 10^4 \text{ sec}^{-1}$	0.141	0.503	1.01	1.09	1.61
Phase <sup>a</sup>	g	g	g	a	b
Temp, $^{\circ}\text{C}$	161.5	166.9	174.4	174.9	174.9
$k \times 10^4 \text{ sec}^{-1}$	1.86	3.08	5.61	6.42	9.01
Phase	g	g	g	a	b
Temp, $^{\circ}\text{C}$	178.0	184.3	196.2		
$k \times 10^4 \text{ sec}^{-1}$	7.82	12.9	34.4		
Phase	g	g	g		

<sup>a</sup> g = gas phase; a = dimethyl-*d*<sub>6</sub> sulfoxide as solvent; b = diphenyl ether as solvent.

For the majority of runs in the gas phase, an initial reactant pressure of 2 Torr was used. However, variation of the initial reactant pressure from 0.8 to 6 Torr did not produce any variation in per cent decomposition for constant reaction time. Similarly, the addition of up to 300 Torr of nitrogen produced no change in the rate of isomerization. Two reaction vessels were used for the gas-phase study, one having a surface to volume ratio eightfold that of the other. Rate constants measured in the packed vessel showed no deviation from an Arrhenius plot of those measured in an unpacked vessel (Figure 1). The data in Table I therefore almost certainly refer to a homogeneous first-order isomerization. The Arrhenius equation of the gas-phase data calculated by the method of least squares is given by

$$k = 10^{13.3 \pm 0.1} \exp(-33,930 \pm 160 \text{ cal}/RT) \text{ sec}^{-1}$$

where the error limits are standard deviations.

## Discussion

Compared to the parent hydrocarbon,<sup>5</sup> the activation energy for the isomerization of 1,4-dichlorobicyclo-

(15) M. L. Poutsma, *J. Org. Chem.*, **33**, 4080 (1968).

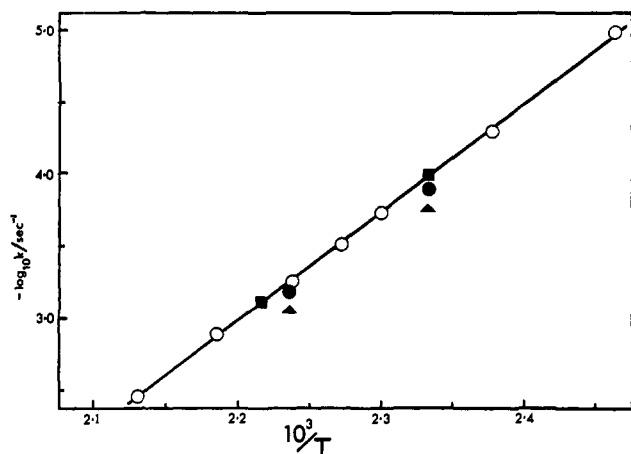
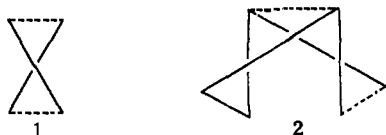


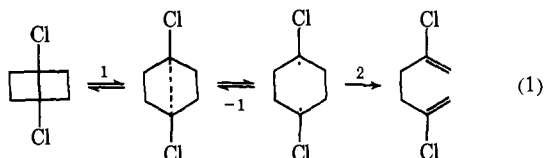
Figure 1. Arrhenius plot for the isomerization of 1,4-dichlorobicyclo[2.2.0]hexane to 1,5-hexadiene: (○) gas phase; (■) gas phase, packed vessel; (●) dimethyl-*d*<sub>6</sub> sulfoxide; (▲) diphenyl ether

[2.2.0]hexane is reduced by 2.1 kcal/mol, whereas within experimental error the Arrhenius *A* factor is unchanged. Equating this *A* factor to  $(ekT/h) \exp(\Delta S^\ddagger/R)$ ,  $\Delta S^\ddagger$  is calculated to be 0 gibbs/mol at 450°K. Unfortunately this value of  $\Delta S^\ddagger$  is consistent with either a concerted mechanism, or the alternate route *via* the intermediate cyclohexane 1,4-diradical. If we compare the symmetry-allowed transition state for cyclobutane ring opening (1) with the corresponding transition state for bicyclo[2.2.0]hexane (2), it is obvious that the mutual twisting of the fused cyclobutane rings imposes severe addition strain and nonbonding interaction on the transition complex.



As discussed in the introductory section, the ratio of concerted to biradical mechanism is a maximum of 1:2 for 7,8-*cis,exo*-dideuteriobicyclo[4.2.0]octane, decreasing to zero for 6,7-dimethylbicyclo[3.2.0]heptane. In these bicyclic systems the bridgehead bond is not broken and hence the strain in the concerted transition complex will be similar to that for cyclobutane. The effect of the additional strain of the bicyclo[2.2.0]hexane transition complex is to ensure that the isomerization will be exclusively by a biradical mechanism.

We may now consider the activation energy in terms of a biradical mechanism (eq 1). Applying the method



of Benson and O'Neal<sup>1,16</sup> to the 1,4-dichlorobicyclo[2.2.0]hexane system,  $\Delta H_1$  is calculated to be 24.9 kcal/mol after correction of  $E_{-1}$  by 1 kcal/mol for the C-Cl gauche interaction.<sup>17</sup> Assuming the H-H and Cl-Cl

(16) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970).

(17) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

1,4-interactions in the parent molecules to be the same, the difference in  $\Delta H_1$  of 3.0 kcal/mol may be defined as the radical stabilization energy of the chlorine atoms. Experimental errors associated with this stabilization energy are  $\pm 1$  kcal/mol for the reference hydrocarbon<sup>5</sup> and  $\pm 0.2$  kcal/mol for this work. We have assigned an error of  $\pm 1$  kcal/mol to both relative comparisons of gauche interactions and 1,4-interactions. (Relevant literature comparisons in support of the values used for these interactions may be obtained from the authors.) Due to the similarity of the reaction coordinates,  $\Delta H_1$  has been assumed to have the same temperature dependence for both compounds. The radical stabilization energy per chlorine atom at 298°K is thus  $1.5 \pm 1.0$  kcal/mol.

Cocks and Frey have reported the Arrhenius parameters for the isomerization of chlorocyclobutane.<sup>18</sup> At 750°K, the activation energy for the decomposition to chloroethylene and ethylene was 2.4 kcal/mol less than that for cyclobutane. As the transition complex for chlorocyclobutane is much "tighter" than that for cyclobutane, application of the appropriate heat capacity corrections would bring the stabilization energy at 298°K into good agreement with that determined in this present work.

Franklin and Huybrechts have discussed the thermochemistry of a number of chloroethyl radicals.<sup>19</sup> Using the enthalpy values in their paper, the C-H bond strengths  $\alpha$  to the chlorine atoms in chloroethane and 1,2-dichloroethane are calculated to be identical at 96.7 kcal/mol. Compared to a primary C-H bond strength in alkanes of 98.0 kcal/mol,<sup>17</sup> this is equivalent to a stabilization energy of 1.3 kcal/mol, in excellent agreement with the experimental results.

The previous discussion has been confined to the Arrhenius parameters measured in the gas phase. We have also measured the rate of isomerization in the liquid phase using both dimethyl sulfoxide and diphenyl ether as solvent. From Figure 1, it may be seen that the rate in dimethyl sulfoxide is *ca.* 10% faster than in the gas phase, whereas the rate in diphenyl ether is *ca.* 60% faster than that in the gas phase. As the rate in the more polar dimethyl sulfoxide is less than that in diphenyl ether ( $\epsilon = 48.9^{20}$  compared to 3.7) the transition complex cannot be more polar than the reactant. At present, we can advance no conclusive reason for the increased rate in the less polar solvent, although it may be noted that Gassman<sup>21</sup> observed no correlation of solvent polarity with reaction rate in a biradical reaction. It may also be noted that a general rate increment of this order of magnitude for solution rates compared to the gas-phase rates appears to be widespread for nonpolar reactions. It has been observed in the isomerization of bicyclo[3.2.0]hept-6-ene by a biradical mechanism,<sup>22</sup> in the isomerization of 1,2-dimethylcyclobutene by a concerted mechanism,<sup>23</sup> and

(18) A. T. Cocks and H. M. Frey, *J. Amer. Chem. Soc.*, **91**, 7583 (1969).

(19) J. A. Franklin and G. H. Huybrechts, *Int. J. Chem. Kinet.*, **1**, 3 (1969).

(20) A. J. Parker, *Advan. Phys. Org. Chem.*, **5**, 173 (1967).

(21) P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1524 (1968).

(22) G. R. Branton, H. M. Frey, D. C. Montague, and I. D. R. Stevens, *Trans. Faraday Soc.*, **62**, 659 (1966).

(23) H. M. Frey, D. C. Montague, and I. D. R. Stevens, *ibid.*, **63**, 372 (1967).

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

## 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

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

chlorine atom is shown to stabilize an  $\alpha$  free radical by  $1.5 \pm 1.0$  kcal/mol. This small stabilization energy is not inconsistent with stabilization energies derived from the 1-chloro-1,4-tetramethylene biradical or the  $\alpha$ -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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## 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  $81.1 \pm 2.0$  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.<sup>1</sup> The former, allowed by orbital symmetry,<sup>2</sup> envisages the simultaneous formation of both bonds (A),<sup>3</sup> 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).<sup>4,5</sup> To these widely disputed alternatives, Woodward and Katz have added a third, a merger of the two mechanisms into a two-stage process (C)<sup>4</sup> (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.<sup>5–7</sup> 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,<sup>8–23</sup> 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–spirpentane 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:  $E_a = 26.0$ ,<sup>10</sup> 23.7,<sup>11</sup> and 26.8 kcal/mol.<sup>12</sup>

(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.*,<sup>15</sup> and an assumed increment of 1.0 kcal/mol for the interaction of a pair of *cis*-1,2 substituents.<sup>16</sup>

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