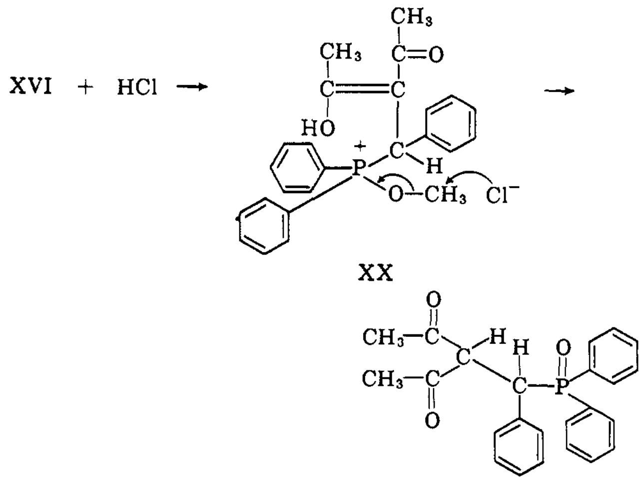
groups of the dipolar structure XIX was approximately 127° in *o*-dichlorobenzene solution.

Ethyl diphenylphosphinite (XIV) gave the corresponding oxyphosphorane XVII. The data are given in Tables I, II, and III. The temperature at which the signals due to the acetyl and the methyl groups on the phospholene ring coalesced to one signal was approximately 20° lower in the case of the ethyl compound XVII than the methyl compound XVII.

The oxyphosphorane XVIII derived from phenyl diphenylphosphinite (XV) is described in the tables. The temperature for the coalescence of the signals due to the acetyl and the methyl protons was at *ca.* 160° in *o*-dichlorobenzene.



XX

XXI, δP^{31} = 31.0 ppm

Although the opening of the ring of derivatives of the 2,2-dihydro-1,2-oxaphospholene-4 heterocycles, II, VIII–X, XVI–XVIII, occurred at relatively high temperatures, the rupture of the ring was extremely rapid under the influence of acids. For example, anhydrous hydrogen chloride converted the phosphinite adduct XVI into the phosphine oxide XXI at low temperatures. The likely intermediate in this reaction is the oxyphosphonium chloride XX.

Experimental Section

The analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Reactions of the Phosphonite and Phosphinite Esters with 3-Benzylidene-2,4-pentanedione. The reactions were carried out by mixing equimolar amounts of the reagents in methylene chloride solution at 20° under anhydrous conditions. The solutions were stirred at room temperature for approximately 12 hr. The solvent was removed under reduced pressure. The residue was analyzed by infrared and by ^1H and ^{31}P nmr spectrometry. The residues were treated with hexane at 0° to achieve crystallization. The analytical samples were obtained by recrystallization from the solvent indicated in Table I. The elemental analyses are given in Table I.

Reaction of the Methyl Diphenylphosphinite–3-Benzylidene-2,4-pentanedione Adduct XVI with Hydrogen Chloride. The phosphorane XVI (3.0 g) in CH_2Cl_2 (20 ml) was treated with anhydrous hydrogen chloride at 20° for 3 min. The solution was treated with ether (50 ml) and the solid (1.3 g, mp 182–184°) was recrystallized from methylene chloride–ether.

Anal. Calcd for $C_{24}H_{23}O_3P$: C, 73.9; H, 5.9; P, 7.9. Found: C, 74.0; H, 6.2; P, 7.9.

The infrared spectrum in CH_2Cl_2 had bands at (μ) 5.88 with shoulder at 5.80, 7.00, 7.40, 8.42, and 8.95. The H^1 nmr spectrum had signals at τ 7.91 and 8.20 due to the two acetyl groups which are magnetically nonequivalent.

Calculated Energies and Geometries along the Reaction Path in Cope Rearrangements

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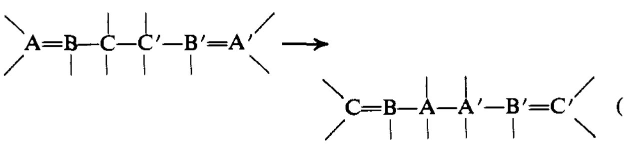
Contribution from the Institute of Physical Chemistry, University of Milan, Milan, Italy. *Received September 13, 1967*

Abstract: A modification and extension of the Westheimer approach have been used to calculate the geometry and energy of cyclopropane, cyclobutane, hexa-1,5-diene, *cis*-1,2-divinylcyclopropane, *cis*-1,2-divinylcyclobutane, *cis,cis*-cyclohepta-1,4-diene, and *cis,cis*-cycloocta-1,5-diene. The geometrical and energetic changes during the pertinent Cope rearrangements were calculated as a function of the degree of advancement of the reaction and reasonable agreement with experiment was found.

The Cope reaction, discovered a long time ago,[3] is a thermal rearrangement that obtains in diallylic systems (eq 1). Experimental results have been extensively reviewed[4] and lead to the following conclusions. The reaction is insensitive to external catalytic influence (including solvent) and follows first-order kinetics. The intramolecular course is demonstrated by the fact that during the rearrangement of a mixture of two diallylic compounds of comparable rates of reaction no exchange of allyl groups is observed. The considerably negative values of the activation entropy (of the order of −12 eu) measured for several Cope rearrange-


$$\mathrm{>A{=}B{-}C{-}C'{-}B'{=}A'<} \longrightarrow \mathrm{>C{=}B{-}A{-}A'{-}B'{=}C'<} \qquad (1)$$

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[1] Institute of Physical Chemistry, University of Catania, Catania, Italy.

[2] Department of Physics, Catholic University Medical School, Rome, Italy.

[3] A. C. Cope and E. M. Hardy, *J. Amer. Chem. Soc.*, 62, 441 (1940).

[4] (a) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, 2, 1 (1963); (b) S. J. Rhoads in "Molecular Rearrangement," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 655; (c) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 2, 115 (1963).

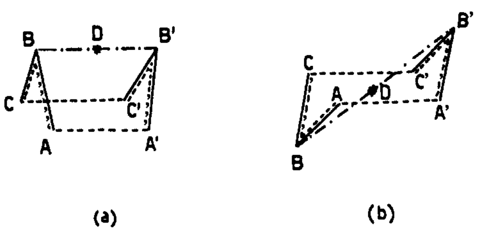

Figure 1. Boat-like (a) and chair-like (b) activated complex.

ments provide a strong argument against a possible cleavage of the diallyl system in the rate-determining step.

The temperature at which the reaction occurs at a measurable rate can be decreased in different ways: introduction of conjugative substituents at position C and/or C′, welding of a strained ring on the C–C′ bond, and favorable preorientation of the two allylic groups by inclusion in a bicyclic rigid structure.[5] All these facts are consistent with the existence of an activated complex in which the two allylic systems must adopt positions in roughly parallel planes with the A and C carbons of each system (primed and unprimed) directly aligned in one of the two possible geometries: *chair-like* or *boat-like* (Figure 1). In the case of 3,4-dimethylhexa-1,5-dienes the geometry of the activated complex has been elucidated by the work of Doering and Roth[6] which shows that the chair-like complex is more stable by about 5.7 kcal/mol.

Theoretical interpretations of these facts have been suggested, based on orbital symmetries[7] or on a HMO perturbation treatment.[8] Both methods have been developed for qualitative work and no attempts of quantitative calculations were presented. The study of chemical reactivity is in fact usually outside the range of applicability of the standard molecular orbital or valence bond theories, even in the case of an intramolecular reaction of hydrocarbons in gas phase. Two oversimplified methods of calculation suggest themselves for problems of this complexity: the extended Hückel method, as formulated by Hoffman,[9] and the Westheimer approach to the quantitative determination of the steric effects in molecules.[10] After preliminary calculations according to the first method had led to rather discouraging results,[11] we turned to the second approach. This method has been developed by Hendrickson and Wiberg[12] and applied by them and by others[13] to the study of the conformations of cycloalkanes. Allinger and coworkers[14] have extended the application to systems in which both σ and π electrons are present. The same method has been used to correlate strain effects with the hydroxymethylene ketone–aldo enol equilibrium,[15] with rates of diimide reduction of olefins,[16] and with rates of solvolysis of bridgehead derivatives.[17] The method has also been used by Scheraga and coworkers[18] to carry out a conformational analysis of several polyamino acids. The same approach has been used for the discussion of the crystal structure of 2-bromo-1,1-di-*p*-tolylethylene[19] and to improve the results of the crystal structure determination of 2-bromo-1,1-diphenylprop-1-ene.[20] The use of calculations of this kind has also been of great help in the determination of the crystal structure of the potassium Meisenheimer salt.[21] Because of the success obtained in many different applications, the Westheimer approach seems to be the most promising tool available at this time for the study of chemical reactivity, and in the present paper it has been applied to the calculation of the geometry and the energy along the reaction path for a few simple molecules undergoing the Cope rearrangement.

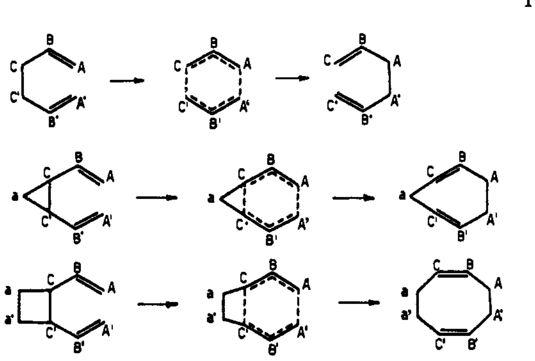

Figure 2. Indexing of atoms before and after rearrangement.

A preliminary report of part of our results has been given;[22] some numerical results presented now show small differences due to different values for some of the constants used in the calculations, but the general conclusions are not affected. We performed the calculations for the Cope rearrangement of hexa-1,5-diene, *cis*-1,2-divinylcyclopropane, and *cis*-1,2-divinylcyclobutane, shown in Figure 2.

Method of Calculation

During the reaction there is rupture of the C–C′ σ bond and making of the A–A′ σ bond. The bond order of the π bonds A–B and A′–B′ changes from 1 to 0 while the order of the π bonds B–C and B′–C′ changes in the reversed sense. Hybridization at carbon atoms B and B′ does not change, while carbon atoms A and A′ change from sp^2 to sp^3 hybridization and carbon atoms C and C′ from sp^3 to sp^2. The order of the σ bonds A–A′ and C–C′ and the hybridization at atoms

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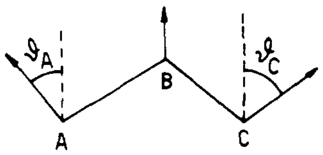

Figure 3. Dihedral angles for the directions of orbitals involved in the π system.

A, A′, C, and C′ are assumed to vary linearly with the degree of advancement λ. The range of variation of λ is of course from 0 to 1 and a scanning of 0.1 was used.

The energy of the molecules has been calculated as the difference in energy between the molecule in a given conformation and a hypothetical molecule with no bond angle or bond stretching strains, no torsional strains, and no steric repulsions and with a given number of single C–C and C–H bonds and double C=C bonds. The total energy difference is given by the following sum

$$E_T = \Delta E_\sigma + \Delta E_\pi + E_c + E_a + E_t + E_{nb} \quad (2)$$

where ΔE_σ and ΔE_π represent the variation in the σ and π electron energies in the part of the molecule site of the reaction, and E_c, E_a, E_t, and E_{nb} represent bond length, bond angle, torsional, and nonbonded interaction strains. For each reaction the calculations were performed for the reactant and the reaction product and in different points along the reaction coordinate, characterized by the degree of advancement λ. For a given λ all bond distances and part of the bond angles were calculated (see below) but the geometry was not completely fixed: three parameters were allowed to vary, *i.e.*, the energy was minimized with respect to them. These parameters (θ_A, θ_C, and γ) are, respectively, the dihedral angles between the axis of local atomic ternary symmetry at A and C carbon atoms and the axis of the p orbital at carbon B, as illustrated in Figure 3, and the angle between the planes A–B–C and A–A′–D where D is the midpoint of the segment B–B′ (see Figure 1a and b). In this way the energy along the reaction path was calculated and hence the energy and the geometry of the activated complex were obtained.

In this respect our calculations show a major departure from the methods previously used in discussing rates of reaction where the geometry of the transition state was obtained by the use of a disposable parameter[16] or assuming a carbonium ion as a model for the transition state.[17] In our calculations we need the values of a number of physical constants for which different values can be found in the literature. The values used in our work and the related references are collected in Table I.

Table I. Bond Lengths, Bond Energies, and Force Constants

Type of bond	Bond length,[a] r_e, Å	Stretching force constant,[b] k, dyn/cm $\times 10^{-5}$	Bond energy E_0, kcal/mol
C–C			
sp^3–sp^3	1.54	4.57[c]	83[d]
sp^3–sp^2	1.52	5.13	87.2[e]
sp^2–sp^2	1.48	6.17[c]	95[c]
C=C			
sp^2–sp^2	1.334	9.57	146[d]
C–H			
sp^3–H	1.108[f]	4.8	96.3[c]
sp^2–H	1.085	5.1	100.5[c]

[a] L. E. Sutton, "Interatomic Distances," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965, unless otherwise stated; see also N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 3966 (1967). [b] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., New York, N. Y., 1945, unless otherwise stated. [c] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960). [d] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publishers, London, 1958. [e] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). [f] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961).

The σ Energy. The first term in the right side of eq 2 has been evaluated at each value of λ, θ_A, θ_C, and γ, assuming that the energy of the bond is proportional to the overlap integral between the orbitals involved. The necessary overlap integrals are evaluated over hybrids of Slater orbitals centered at the proper distance and pointed to the proper directions according to standard formulas.[23] Calculations of distances were performed as explained later in the Geometry section. It is

$$\Delta E_\sigma = E_{te}\left(\frac{\lambda S_{AA'} + (1 - \lambda)S_{CC'}}{S_{te}} - 1\right) \quad (3)$$

where E_{te} is the energy of a C_{sp^3}–C_{sp^3} single bond and S_{te} is the overlap integral between two sp^3 hybrids pointing to each other and centered 1.54 Å apart.

The Compression Energy. The bond length strain has been evaluated for the C_{sp^2}=C_{sp^2}, C_{sp^3}—C_{sp^2}, C_{sp^2}—C_{sp^2} (in ethylene and benzene) bonds according to the Morse formula

$$E = E_0(1 - e^{-a(r - r_e)})^2 \quad (4)$$

where $a = \sqrt{k/2E_0}$ and the values for all the constants are found in Table I. We prefer to consider the compression of the double bond as a whole instead of splitting it in a σ and π system as the C_{sp^2}–C_{sp^2} σ bond is perhaps the one for which the available data are less reliable. For example the values obtained by Allinger, *et al.*,[14] for r_e and k of this bond (1.513 Å and 12.825 $\times 10^5$ dyn/cm, respectively) are considerably different from the corresponding values in Table I. Along the rearrangement E_c is given by the sum of four terms calculated according to eq 4, two for the double bonds and two for the C_{sp^3}–C_{sp^2} single bonds.

The π Energy. ΔE_π has been evaluated as the HMO (Hückel molecular orbital) delocalization energy. The value of β_0, the resonance integral for two parallel p orbitals centered at a distance r_e = 1.334 Å, has been estimated to be equal to −30 kcal/mol. For example, in ethylene if we calculate $E_{\text{double bond}} = E_{\text{single bond}} + 2\beta_0$ and the energy of the C_{sp^2}–C_{sp^2} single bond is taken from Table I and corrected according to eq 4 for compression from 1.48 to 1.334 Å, we obtain the reasonable result

$$E_{\text{double bond}} = -95 + 13 - 60 = -142 \text{ kcal/mol}$$

We need however to evaluate the integral β for different situations, in which the distance is changed and the orbitals are not pure p but s–p hybrids and are not parallel.

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Besides carbon atoms A and A′, C and C′ have just one orbital each to contribute both to the σ bond between them and to the π bond with atoms B or B′, so the exchange phenomena in the adjacent σ and π bonds are synchronized and β should take account of this. For this reason we felt that an empirical dependence of β from r should be found, and we used the following function whose validity is limited to the range $r = 1.334$ Å$(\beta = \beta_0)/r = 1.52$ Å$(\beta = 0)$

$$\beta = \beta_0(1 - 28.9(r - 1.334)^2) \qquad (5)$$

The consequences of the use of this function in connection with eq 4 have been checked in a calculation on the benzene molecule. The energy of benzene is given by $E_T = E_\pi + E_c = 8\beta + 3E_1 + 3E_2$, where E_1 and E_2 are the compression energies of single and double C_{sp^2}–C_{sp^2} bonds. E_T is a function of r and from the condition $d(E_\pi + E_c)/dr = 0$ an equilibrium distance $r = 1.396$ Å is found in nice agreement with the experimental value (1.393 − 1.397 Å[24]). The energy calculated at $r = 1.396$ Å is −195.06 kcal/mol resulting in a stability of −15.1 kcal/mol with respect to a structure with alternating bond lengths, in agreement with the result obtained by Allinger, *et al.*,[14] that is, −15.5 kcal/mol. In this and in subsequent calculations the exchange integral for an isolated double bond has been arbitrarily considered always equal to β_0, that is, independent of the bond length. This assumption is only in part justified by the results obtained for benzene and by the fact that a rough estimation of β_0 has been accepted.

In our molecules two pseudo-allylic systems are present, and the HMO delocalization energy for the molecules is given by

$$\Delta E_\pi = -120\{\sqrt{\beta_{AB}^2 + \beta_{BC}^2} - 1\} \qquad (6)$$

with β_{AB} and β_{BC} calculated according to eq 5. ΔE_π is apparently a function of r_{AB} and r_{BC} but these in turn are dependent upon θ_A, θ_C, and, through the hybridization, upon λ. The evaluation of the π energy by the empirical Hückel method is perhaps the weakest part of our treatment, and more refined calculations in the Pariser–Parr approximation as used by Allinger, *et al.*,[14] would be more appropriate.

Bending Energy. This energy appears in the cyclopropane and cyclobutane derivatives and in *cis,cis*-cyclohepta-1,4-diene and is evaluated according to the formula

$$E = E_{te}(S/S_{te}) \qquad (7)$$

Here our procedure is at variance with the methods previously used.[11,12,14,17] but our angular deformations are high enough to be out of the range of validity of the commonly used parabolic functions.

As a test of eq 7 calculations have been performed for the highly strained cyclopropane and cyclobutane molecules (see Results).

Torsional Energy. For the bonds in the allylic systems the following approach has been used. Because of the lack of information about the existence and the nature of the torsional barriers from the σ systems in double bonds,[14] at each value of $\lambda \leqslant 0.5$ the A–B (and A′–B′) bond has been considered in the calculation of torsional energies a pure double bond and the B–C (and B′–C′) a pure single bond. For $\lambda > 0.5$ the role of the two bonds has been reversed. The torsional energy around double bonds has been ignored and around single bonds has been evaluated by the formula

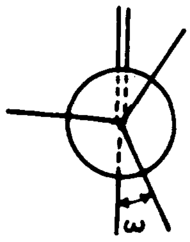

Figure 4. Torsional angle around a C_{sp^3}–C_{sp^2} bond.

$$E = (1.98/2)(1 + \cos 3\omega) \qquad (8)$$

where the angle ω is defined as in Figure 4. The height of the barrier in propylene[25] has been used in eq 8. The torsional energy for the full C–C bonds in the cyclopropane and cyclobutane rings has been calculated by means of a modification of the formula given by Scott and Scheraga[26]

$$E = \frac{K}{18 \sin^6 109.47} \times \left[\sum_{i=1}^{3}\sum_{j=1}^{3} \sin^3\theta_i \sin^3\theta_j (1 + \cos 3\omega_{ij})\right] \qquad (9)$$

where ω_{ij} are the angles between the projection of the directions of the orbitals starting from C_i and C_j on a plane perpendicular to the C_i–C_j bond site of the torsion; θ_i and θ_j are the angles between this bond and the direction of the orbitals used in the adjacent bonds; K is the barrier height and varies with the hybridization of the atoms at the two ends of the bond: $K = 1.98$ kcal/mol for a C_{sp^3}–C_{sp^2} bond, and $K = 2.80$ kcal/mol[12a] for a C_{sp^3}–C_{sp^3} bond. For the σ bond with order less than 1 (that is, A–A′ and C–C′) K has been assumed to be a function of the bond length r

$$K = 3.04r^2 - 15.19r + 18.99 \text{ kcal/mol} \qquad (10)$$

This gives $K = 2.80$ kcal/mol for $r = 1.54$ Å, $K = 0$ and $dK/dr = 0$ for $r = 2.52$ Å (the C_1–C_3 distance in propane). Through eq 9 with K given by eq 10 we verified for the case of hexa-1,5-diene, both along the chair-like and boat-like (transition state) reaction path, that the sum of torsional energies around the A–A′ and C–C′ bonds remained approximately constant for all values of λ. We decided to keep this value constant along all the reactions, that is, $E = 2.80$ kcal/mol for the boat-like path and $E = 0$ kcal/mol for the chair-like path.

Nonbonded Interactions. This energy has been calculated only for distances less than the sum of the van der Waals radii (C····C = 3.2 Å, C····H = 2.8 Å, and H····H = 2.5 Å). As usual in work of this kind,[17] 1–3 interactions were neglected (a rationalization for this practice can be found in a work of Bartell[27]). However for cyclobutane the calculations were performed neglecting or including C_1····C_3 interactions

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[25] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, 27, 868 (1957).

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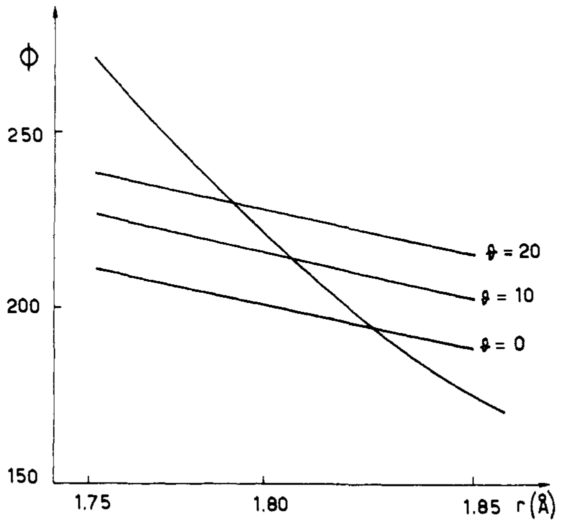

Figure 5. Effective overlap curves for the σ bonds at $\lambda = 0.5$ and $\gamma = 70$ (boat-like geometry).

and for *cis*-1,2-divinylcyclobutane the effect of C–a′ and C′–a interactions has been considered.

The nonbonded energy has been calculated with the formula

$$E_{ij} = -Ar^{-6} + Be^{-Cr} \tag{11}$$

summing over all the interacting pairs. For the choice of the parameters appearing in eq 11 a wide range of possible values has been suggested;[12,17,28,29] we used the values given by Hendrickson.[12a]

Geometry. The C–H distances have been assumed to vary linearly with the hybridization at the carbon atom. The C–C distances given in Table I were used for integer bonds, except in the cyclopropane and cyclobutane rings when the experimentally determined values,[30] 1.52 and 1.56 Å, respectively, were used. Along the reaction path of *cis*-divinylcyclopropane the C–a and C′–a bonds are maintained at 1.52 Å. Along the reaction path of *cis*-divinylcyclobutane the a–a′ distance varies linearly with λ from 1.56 to 1.54 Å, and the C–a and C′–a′ distances from 1.56 to 1.52 Å. To find the length of bonds with noninteger bond order the concept of *effective overlap* has been used. This is based on the generally accepted idea, both in the scope of MO[31] and VB[32] theories, that bonding is due to an increase of electron density in the region between the bonded atoms and that bond length is related to bond energy.

A rough measure of bond energy is given by the overlap integral for the orbitals used in the bond so that a strong bond, with a short bond length, can be obtained with the use of *good* orbitals; with *bad* orbitals, *i.e.*, with orbitals with an inconvenient hybridization or not directly pointing to each other, a higher bond order is needed to obtain the same electron density in the *right* position of space (the same bond energy and the same bond length). There are in fact three distances to be evaluated since we preserve a plane of symmetry along the boat-like path and a C_2 axis along the chair-like path.

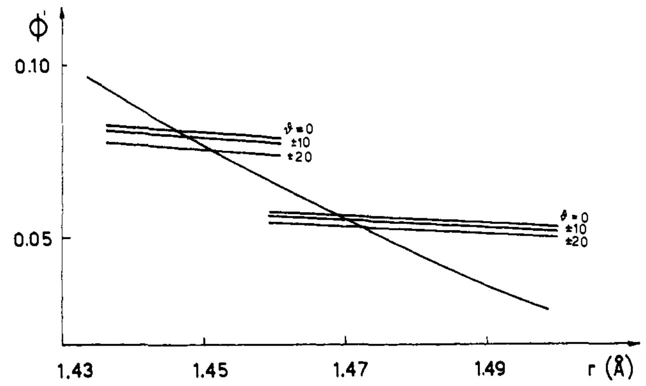

Figure 6. Effective overlap curves for the π bonds at $\lambda = 0.4$ (upper family of curves) and at $\lambda = 0.3$ (lower family of curves).

To find the A–A′ and C–C′ distance at each value of λ we start with the four orthonormal hybrids at each carbon atom, assumed to change their hybridization linearly with λ Three hybrids at each atom are equivalent, that is, identical except for their orientation in the space. They have the form

$$\psi = \frac{1}{2}\left[\sqrt{1 + \frac{\lambda}{3}}\varphi_s + \sqrt{3 - \frac{\lambda}{3}}\varphi_p\right] \tag{12}$$

One orbital is different, with the form

$$\psi^* = \frac{1}{2}[\sqrt{1 - \lambda}\varphi_s + \sqrt{3 + \lambda}\varphi_p] \tag{13}$$

In eq 12 and 13 φ_s and φ_p are Slater 2s and 2p orbitals at the proper carbon atom. From the orthonormality conditions the angles between orbitals ψ and ψ^* can be calculated at each λ. The orbital ψ^* is used for the formation of the σ bonds A–A′ and C–C′ and for the π bonds in the allylic systems. Also at each λ the amount of electrons available for the formation of bonds A–A′ and C–C′ is known, being related to the bond numbers $n_{A-A'} = \lambda$ and $n_{C-C'} = 1 - \lambda$. The effective overlap is defined as the product of the overlap integral between the two orbitals involved (for example, the ψ^*'s at C and C′) times the bond number (for example, $n_{C-C'}$). For each value of λ, θ_C (or θ_A), and γ we can calculate the *effective overlap* $\Phi = Sn$ as a function of the distance C–C′ (or A–A′). We obtain in this way a set of curves that give, for a fixed value of λ, θ and γ, Φ as a function of *r*. For the case of two tetrahedral hybrids pointing towards each other we can calculate the overlap as a function of *r*. We can also follow Pauling[33] and make use of a formula that gives the bond length for bonds of this kind as a function of the bond number (for bond number <1)

$$r = 1.54 - 0.297 \ln n \tag{14}$$

For a given *n* we can calculate *r* and then *S* for the special bond and obtain the curve that gives $\Phi = Sn(r)$ as a function of *r*. If we have this curve on the same diagram of the curves of Φ for the A–A′ and C–C′ bonds, the crossing with the curve of the desired λ, θ, and γ gives the A–A′ or C–C′ bond lengths. An example of this family of curves is given in Figure 5.

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[29] I. Fischer-Hjalmars, *Tetrahedron*, **19**, 1805 (1963).

[30] J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

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[32] R. Mcweeny, *Proc. Roy. Soc.* (London), **A223**, 63 (1953).

[33] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 255.

The same procedure is used to evaluate the A–B (A′–B′) and B–C (B′–C′) distances. The effective overlap is this time independent from the angle γ. The overlap integral is between an orbital ψ^* and a pure p orbital at B (or B′). The reference curve is obtained as $\Phi' = S'n'(r)$, where S' is the overlap integral between two parallel pure p orbitals at the distance obtained by the formula

$$r = 1.52 - 0.264 \ln n' \qquad (15)$$

where $n' = 1 + n_\pi$. Equation 15 gives $r = 1.334$ for $n_\pi = 1$. We assume $n_{\pi\text{A-B}} = 1 - \lambda$ and $n_{\pi\text{B-C}} = \lambda$. This of course is not exact. After the calculation of the π energy, the π-bond order should be calculated and the calculation should be repeated to consistency after proper modification of eq 15. This has not been done since we verified in a few examples that differences between self-consistent bond orders and the starting n_π values are small. The effective overlap for these bonds is now dependent on λ and θ_A or θ_C. An example of this family of curves is shown in Figure 6. The bond angles HCH and HCC have been determined assuming the hydrogen atoms to lie in the direction of maximum strength of the carbon orbital used in the bond. Trigonal and tetrahedral angles have always been assumed to be equal to 120 and 109.47°.

In hexa-1,5-diene (boat- or chair-like form), *cis*-divinylcyclopropane, and *cis*-1,2-divinylcyclobutane the vinylic side chains were allowed to rotate in order to assume the minimum $E_\text{t} + E_\text{nb}$ energy. Of course the boat-like conformation of the hexa-1,5-diene has also 2.8-kcal/mol torsional energy around the C–C′ bond. In divinylcyclopropane and -butane atoms a or a and a′ were located in the plane of the ψ orbitals used in bonding C and C′ with a or a and a′. For cyclopropane and cyclobutane both experimental and theoretical HCH angles were tried. For cycloheptadiene no strainless geometry is possible. The strain has been assumed to be all of angular type. A plane of symmetry has been assumed, through atom a and the midpoint of the A–A′ bond and normal to the A–A′ bond. All the angular deformations were located at a, A, and A′ (Figure 7). For cyclooctadiene two conformations are possible: a chair-like and a boat-like. The second case undergoes pseudo-rotation, as defined by Hendrickson.[12a] The amount of pseudo-rotation is defined through the torsional angle around a single bond adjacent to a double bond ω_{Ca}. Two values of the other different torsional angles correspond to each value of this angle and so two different geometries.

Programming. The calculations were performed on an IBM 1620 (20K) computer, using FORTRAN programs. The calculations at $\lambda \neq 0$ and $\lambda \neq 1$ were organized in different steps: (a) determination of geometry, given λ, θ_A, θ_C, and γ (this step includes the calculation of overlap integrals, effective overlap, and interatomic distances); (b) calculation of the different terms in the right-hand side of eq 2; (c) minimization of the total energy through numerical evaluation of the derivatives with respect to θ_A, θ_C, and γ. When λ equals 0 or 1 *ad hoc* programs were used.

Results and Discussion

Since two molecules considered in this study contain small rings we first checked our method of calculation using cyclopropane and cyclobutane.

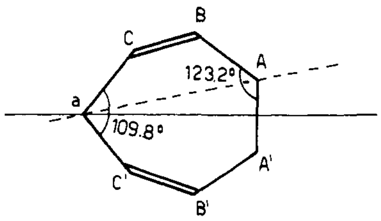


Figure 7. Minimum-energy geometry of hepta-1,4-diene.

Cyclopropane. The calculations were performed for two different geometries. (a) The experimental geometry was assumed.[30] The hybridization at the carbon atoms was changed in order to have two hybrids pointing in directions with an angle of 117°. The four orbitals are then: $\Psi_1 = \Psi_2 = 0.5588\varphi_\text{s} + 0.8293\varphi_\text{p}$ (to be used for the C–H bonds with HCH = 117°); $\Psi_3 = \Psi_4 = 0.4333\varphi_\text{s} + 0.9013\varphi_\text{p}$ (to be used for the C–C bonds with CCC = 103.4°). With these orbitals the angle strain energy was calculated (see eq 7). The torsional energy was calculated by the Scott and Sheraga method using $K = 2.8$ kcal/mol (eq 9), and in the calculation of nonbonded interactions the geminal hydrogen pairs were not considered. (b) The geometry assumed here (HCH = 109.47°, $r_{\text{C–C}} = 1.52$ Å, $r_{\text{C–H}} = 1.108$ Å) allows sp^3 hybridization at the carbons. The repulsion energy has been evaluated with or without C····H interactions, since it is not clear if such 1–3 interactions should be included or not for molecules with small rings. The results are collected in Table II. The experimental total strain is 27.6 kcal/mol.[30]

Table II. Strain Energies in Cyclopropane and Cyclobutane (kcal/mol)

Compd	E_a	E_t	$E_{\text{H}\cdots\text{H}}$	$E_{\text{C}\cdots\text{H}}$	$E_{\text{C}\cdots\text{C}}$	E_T
			Cyclopropane			
Case a	17.55	6.63	0	4.80		28.98
Case b$_1$	15.57	6.39	0	3.72		25.68
Case b$_2$	15.57	6.39	0			21.96
Exptl						27.6
			Cyclobutane			
Case a	17.28	11.40	0.02	7.68	6.44	42.82
Case b$_1$	10.24	10.76	0	6.08	6.44	33.52
Case b$_2$	10.24	10.76	0		6.44	27.44
Case b$_3$	10.24	10.76	0			21.00
Exptl						26.0

Cyclobutane. Both experimental (HCH = 114°) and assumed geometries were considered (case a and b) and calculations were carried out along the same lines as for cyclopropane. In case b three possibilities were allowed corresponding to inclusion or not of C$_1$····C$_3$ and C$_1$····H$_3$ interactions. The results are shown in Table II. The experimental total strain is 26 kcal/mol.[30] The results for both cyclopropane and cyclobutane show that the use of the regular sp^3 hybridization at the carbons is advisable.

Hexa-1,5-diene. This molecule in the most stable conformation has a center of symmetry and no strains in our approximation. To assume the best conformation for reaction along the boat-like path there is a torsional barrier of 2.8 kcal/mol; besides there are small rotations of the vinyl groups around the B–C and

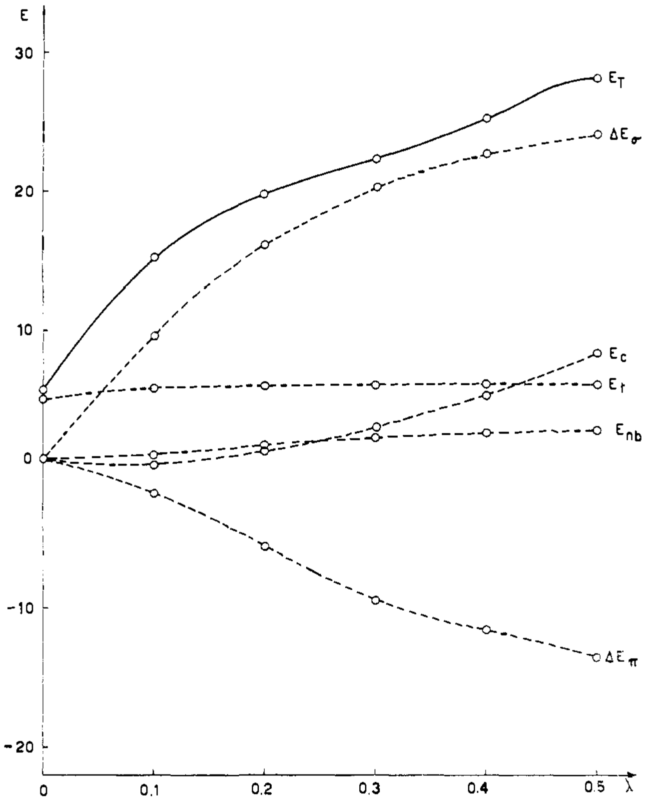


Figure 8. Partial and total energies for the hexa-1,5-diene rearrangement along the boat-like path.

B′–C′ bonds to minimize $E_t + E_{nb}$, both for the chair-like and boat-like reaction path. The *best* geometry at $\lambda = 0$ is shown in Table III. Because of symmetry the two reaction paths for this molecule were investigated only up to $\lambda = 0.5$. The activated complex is at $\lambda = 0.5$ (this was checked with supplementary calculations at $\lambda = 0.45$ and $\lambda = 0.48$). The geometry of the activated complex is shown in Table IV, while the energies along the path of the reaction are collected in Tables V and VI, and shown in Figures 8 and 9. The activation energies, at 0°K and apart from zero-point energy differences, are 28.1 kcal/mol for the boat-like activated complex and 22.8 kcal/mol for the chair-like. The difference (5.3 kcal/mol) is in the right direction and compares favorably with the experimental value for 3,4-dimethylhexa-1,5-dienes.[6] An experimental value of the activation energy for 1,1-dideuteriohexa-1,5-diene is known: $\Delta E^{\ddagger} = 35.5$ kcal/mol.[34]

Table III. Geometries at $\lambda = 0$ (distances in Å, angles in degrees)

Compound	AA′	BB′	CC′	BCC′	ω_{BC}
Hexa-1,5-diene					
Boat-like	2.900	2.550	1.54	109.47	87.6
Chair-like	3.000	2.924	1.54	109.47	88.9
cis-1,2-Divinylcyclopropane	4.018	2.896	1.52[a]	120.0	104.7
cis-1,2-Divinylcyclobutane	4.674	2.683	1.56[b]	114.0	136.6

[a] $d_{Ca} = d_{C'a} = d_{CC'}$. [b] $d_{Ca} = d_{aa'} = d_{C'a'} = d_{CC'}$.

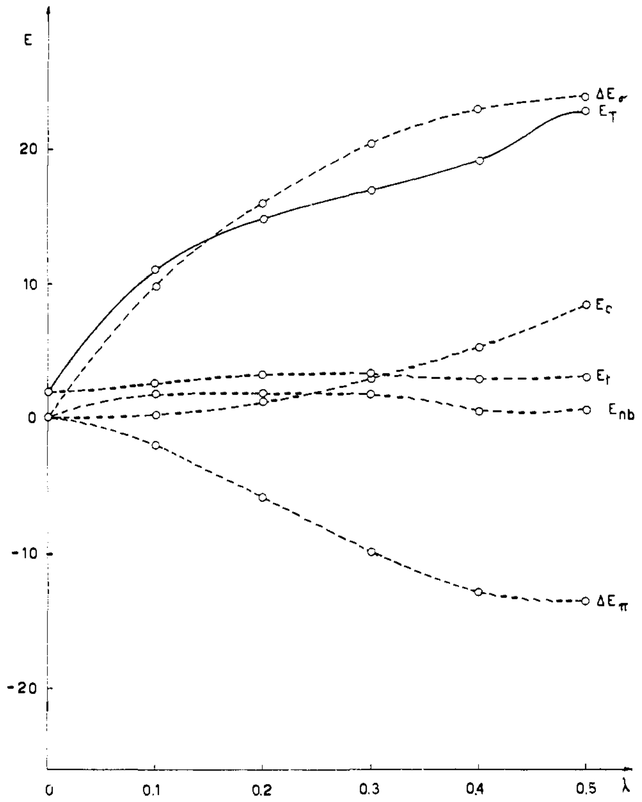
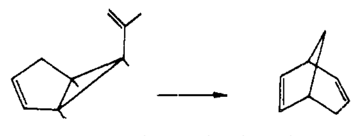


Figure 9. Partial and total energies for the hexa-1,5-diene rearrangement along the chair-like path.

***cis*-1,2-Divinylcyclopropane.** The results obtained for cyclopropane and cyclobutane would suggest the inclusion of C····H interactions for divinylcyclopropane and the exclusion of these interactions for divinylcyclobutane. For sake of consistency C····H interactions were excluded for both molecules. The most stable conformation of divinylcyclopropane in our approximation is the one given in Table III. It is 22.1 kcal/mol less stable than the *hypothetical* unstrained molecule. Consideration of the molecular geometry involved in this rearrangement (and in the rearrangement of *cis*-1,2-divinylcyclobutane) leads to the conclusion that only the boat-like reaction path is available. The results are collected in Table VII and Figure 10. The activated complex is found close to $\lambda = 0.5$. The activation energy is 17.2 kcal/mol at 0°K. This can only be compared with a value of $\Delta H_{313}^{\ddagger} = 22.3$ kcal/mol reported for the Cope rearrangement of *cis*-6-vinylbicyclo[3.1.0]hex-2-ene.[35] Our product is *cis,cis*-cyclohepta-1,4-diene; the calculated minimum of energy obtains with the geometry given in Figure 7; the reaction enthalpy, at 0°K and apart from zero-point energy effects, is −18.7 kcal/mol.



***cis*-1,2-Divinylcyclobutane.** For this molecule and its reaction the calculations were first performed without inclusion of $C_1 \cdots C_3$ interactions. An alternative set of energies was obtained adding the C····a′ and C′····a repulsion energies without changing the

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(34) W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, 7, 397 (1966).

(35) J. M. Brown, *Chem. Commun.*, 226 (1965).

Table IV. Geometries at $\lambda = 0.5$ (distances in Å, angles in degrees)

Compound	AB	BC	CC′	AA′	BB′	γ	θ_A	θ_C
Hexa-1,5-diene								
Boat-like	1.418	1.418	1.782	1.782	2.278	84.3	7.5	7.5
Chair-like	1.418	1.418	1.782	1.782	2.535	86.5	5	5
cis-1,2-Divinylcyclopropane	1.424	1.421	1.780	1.778	2.442	79.3	20	−10
cis-1,2-Divinylcyclobutane	1.423	1.421	1.829	1.781	2.461	79.3	15	10

Table V. Minimized Parameters and Energies of Hexa-1,5-diene along the Boat-Like Path (units of degrees and kcal/mol)

λ	γ	θ_A	θ_C	E_{nb}	ΔE_π	E_c	ΔE_σ	E_t	E_T
0	89.9	0	3	0.72				5.03	5.75
0.1	86.3	10	10	1.15	−1.77	0.37	9.60	5.87	15.22
0.2	85	10	10	1.73	−5.51	1.38	16.17	5.98	19.75
0.3	85	10	10	2.24	−9.39	3.07	20.35	6.09	22.36
0.4	85	10	10	2.61	−11.56	5.38	22.73	6.21	25.37
0.5	84.3	7.5	7.5	2.83	−13.48	8.46	24.16	6.16	28.13

Table VI. Minimized Parameters and Energies of Hexa-1,5-diene along the Chair-Like Path (units of degrees and kcal/mol)

λ	γ	θ_A	θ_C	E_{nb}	ΔE_π	E_c	ΔE_σ	E_t	E_T
0	88.4	0	0.1	0.72				1.96	2.03
0.1	86.5	0	5	0.18	−1.96	0.34	9.89	2.60	11.05
0.2	84.7	0	10	0.19	−5.85	1.32	16.01	3.18	14.85
0.3	83	0	10	0.18	−9.86	2.98	20.47	3.29	17.06
0.4	86.5	5	5	0.58	−12.86	5.38	23.07	3.0	19.17
0.5	86.5	5	5	0.71	−13.48	8.46	23.96	3.16	22.81

geometry. The most stable conformation (see Table III) has a strain energy of 22.5 or 28.7 kcal/mol, respectively. The results and the two energy curves are reported in Table VIII and Figure 11. The calculated activation energy is 18.5 or 16.7 kcal/mol, respectively. The activated complex again occurs for $\lambda \cong 0.5$. The activation energy for this reaction has been calculated from published data[36] to be 23.8 kcal mol in the 65–108° range of temperature. The reac-

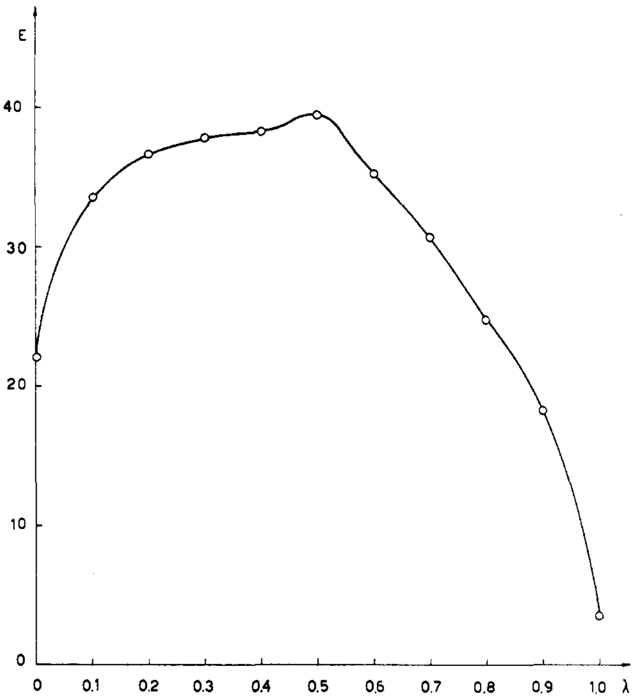

Figure 10. Total energy for the divinylcyclopropane rearrangement.

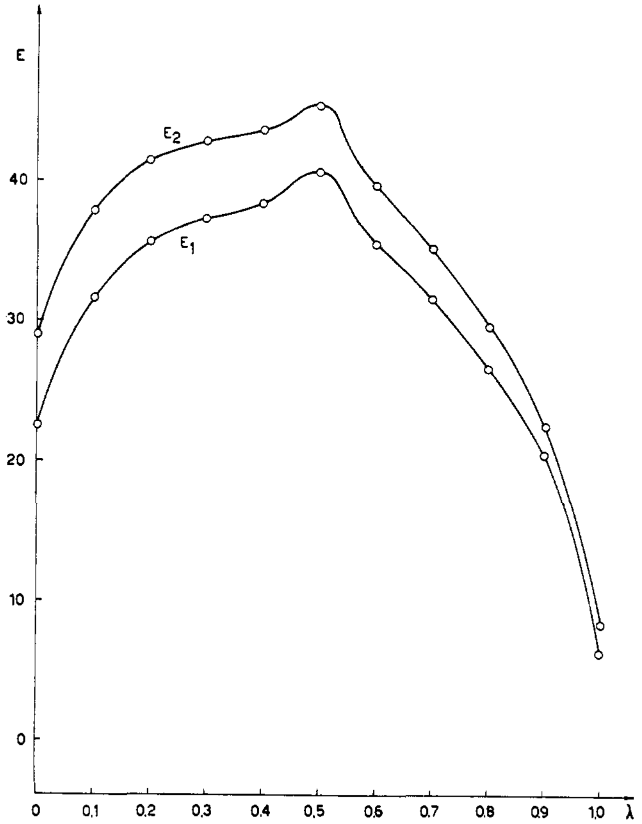

Figure 11. Total energy for the divinylcyclobutane rearrangement without (E_1) and with (E_2) inclusion of C–a′ and C′–a repulsion energies.

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[36] G. S. Hammond and C. D. deBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

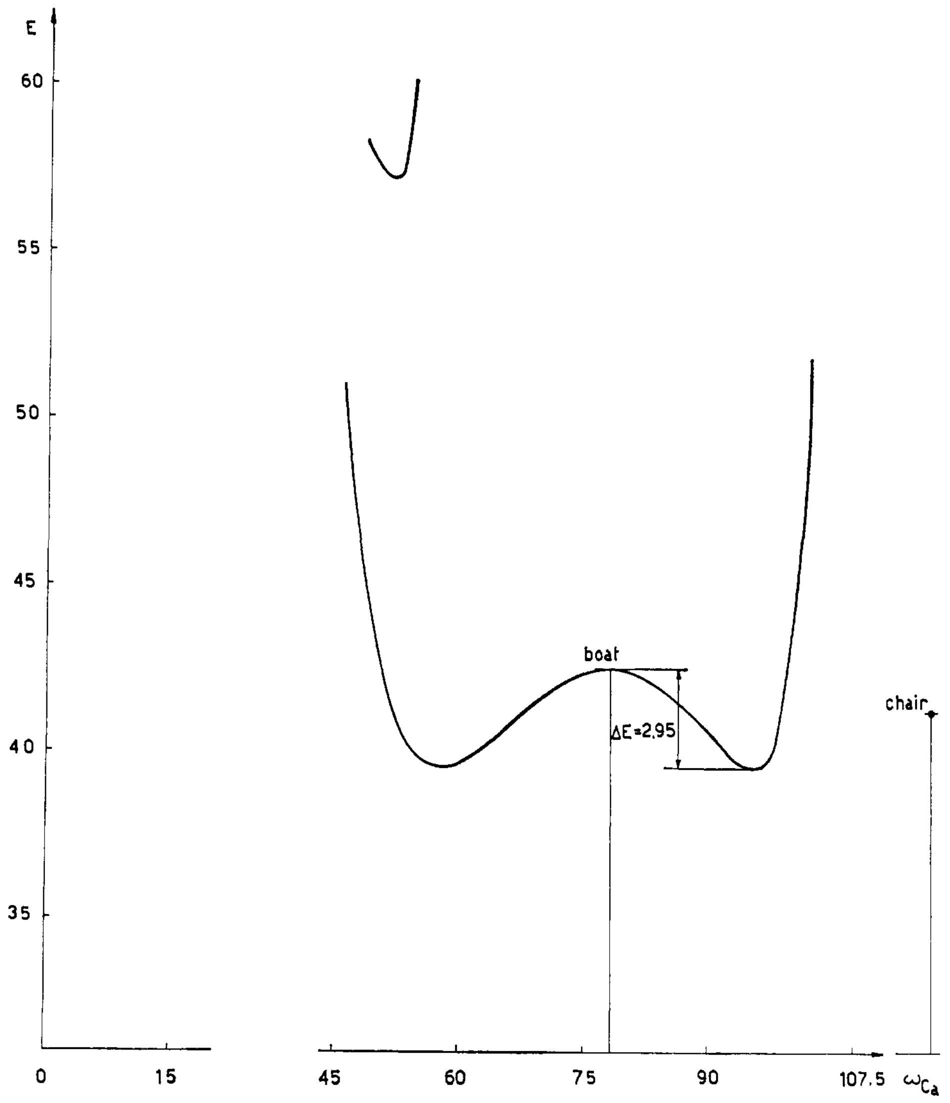

Figure 12. Calculated energies and pseudo-rotation of cyclooctadiene.

tion product is *cis,cis*-cycloocta-1,5-diene. This can exist in a boat and in a chair form, the first one undergoing pseudo-rotation along which a C_2 axis is preserved. Bond angles and distances do not change during the pseudo-rotation. The geometry and the energy of the chair and the boat and the minimum energy conformations are reported in Table IX. In this calculation all repulsion energies were included. The energy of the boat form during the pseudo-rotation is reported in Figure 12 as a function of ω_{Ca}. Two curves appear in the figure. They are shown only in part since for

Table VII. Minimized Parameters and Energy for the Reaction of *cis*-1,2-Divinylcyclopropane (units of degrees and kcal/mol)

λ	γ	θ_A	θ_C	E_T
0				22.14
0.1	85.0	15	−10	33.60
0.2	83.6	15	−10	36.69
0.3	82.2	15	−10	37.78
0.4	80.8	15	−10	38.20
0.5	79.3	20	−10	39.37
0.6	77.8	20	−10	35.24
0.7	77.8	20	−10	30.70
0.8	76.2	20	−15	24.69
0.9	74.6	20	−25	18.19
1				3.47

Table VIII. Minimized Parameters and Energy for the Reaction of *cis*-Divinylcyclobutane (units of degrees and kcal/mol)

λ	γ	θ_A	θ_C	E_1[a]	E_2[b]
0				22.25	28.69
0.1	79.3	15	15	31.69	37.82
0.2	80.8	15	15	35.56	41.40
0.3	80.8	15	10	37.26	42.71
0.4	80.8	15	10	38.42	43.51
0.5	79.3	15	10	40.72	45.38
0.6	79.3	20	10	35.52	39.71
0.7	79.3	20	5	31.61	35.20
0.8	79.3	20	5	26.62	29.56
0.9	79.3	20	0	20.48	22.50
1				6.51	8.23

[a] Without $C_1 \cdots C_3$ interactions. [b] With $C_1 \cdots C_3$ interactions.

Table IX. Torsional Angles and Energies for *cis,cis*-Cycloocta-1,5-diene

Conformation	ω_{Ca}	$\omega_{aa'}$	$\omega_{a'C'}$	E, kcal/mol
Boat	78.2	0	−78.2	42.46
Minimum	58.0	23.2	−95.0	39.51
Chair	−78.2	116.0	−78.2	41.20

Table X. Activation Entropies (in eu)

Compound	Geometry of activated complex	$\Delta S^{\ddagger}$ at 273°K	$\Delta S^{\ddagger}$ at 423°K	$\Delta S^{\ddagger}$ at 573°K
Hexa-1,5-diene	Chair-like	−12.50	−16.58	−16.99
Hexa-1,5-diene	Boat-like	−12.65	−16.71	−17.13
cis-1,2-Divinylcyclopropane	Boat-like	−5.50	−8.46	−8.60
cis-1,2-Divinylcyclobutane	Boat-like	−6.60	−10.00	−10.34

certain ranges of values of ω_{Ca} two or more hydrogen atoms come so close that their interaction causes a tremendous increase of E_{nb}. The two curves correspond to the two pairs of values of $\omega_{aa'}$ and $\omega_{a'C'}$ corresponding to each value of ω_{Ca}. The energy of the chair is also shown in Figure 12, for comparison. The reaction enthalpy at 0°K turns out to be $\Delta H_0° = -18.7$ or -23.4 kcal/mol. Calorimetric work is in progress[37] to obtain an experimental result for comparison.

Since our method allows the determination of the geometry and bond orders in the activated complex for these reactions, taking advantage of the fact that only integer or half-integer bond numbers occur, for which the relevant data are available, we calculated the activation entropies for the reactions I–III (Figure 2) according to the standard statistical mechanics method.[38] The results are collected in Table X. The only available experimental result for the reaction of divinylcyclobutane, calculated from published data,[36] is $\Delta S^{\ddagger} = -11.7$ eu at 373°K.

From the general outcome of our results it can be said that satisfactory agreement with experimental data obtains. These calculations support the previously proposed mechanism for the Cope rearrangement and allow a quantitative determination of the geometry of the activated complex with the presumed general shape. In particular, it is good that activation energy for the cyclobutane and cyclopropane derivatives are comparable and both are lower than the values for hexa-1,5-diene. Besides the two values for hexa-1,5-diene chair- and boat-like activated complex are in the right order and with the expected difference. Of course these results are far from being definitive owing to the many approximations included and the use of many physical constants. Further investigation should be carried out to find more rigorous and detailed ways of calculation. Nevertheless they seem to point an effective way to attack the problem of quantitative prediction of chemical reactivity.

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The Dimerization of Styrene[1]

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Received October 11, 1967

Abstract: The thermal polymerization of styrene at 150° gives both higher polymers and a mixture of dimers in largely independent reactions. Eleven C_{16} hydrocarbons have been identified in the dimer fraction. The proportions of these "dimers," the ratio of "dimer" to higher polymer, and the over-all rate of reaction depend on the promoter or inhibitor employed; iodine, sulfur, 2,4,6-trinitrobenzene, picric acid, and ultraviolet light have been tested. The uncomplicated dimerization is mostly a nonchain reaction, giving first 1,2-diphenylcyclobutane and 1-phenyltetralin. Several 1,3-diphenylbutenes arise from acid (or high iodine) catalysis or from free-radical chain reactions. Some of these butenes are hydrogenated to 1,3-diphenylbutane by 1-phenyltetralin, which is thus dehydrogenated to 1-phenyl-1,2-dihydronaphthalene and 1-phenylnaphthalene. Iodine catalyzes the formation of 1-phenyltetralin and sulfur promotes formation of 2,4-diphenyl-1-butene. The latter is also the lowest oligomer resulting from chain transfer of styrene with bromobenzene solvent (with little incorporation of solvent). From these results, new mechanisms for thermal initiation of polymerization and for chain transfer with aromatic solvents are proposed.

Previous work[2] on the thermal polymerization of styrene in refluxing bromobenzene has indicated the presence of two independent reactions. One is the well-known polymerization by a free-radical chain mechanism, with an apparent order near 2.5. The low polymer formed by this mechanism averages nearly one double bond per molecule. The other reaction is bimolecular and nonchain. It leads to a dimer fraction that is more than 90% saturated and therefore cyclic. The earlier work[2] also showed that more dimer could be obtained by using an inhibitor (picric acid) than a diluent to retard the chain reaction. The primary object of the present work was to identify the dimer. However, the infrared absorption of the dimer fraction changed as the inhibitor was changed. This paper shows how the dimer fractions were resolved into several isomeric

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(1) Earlier and shorter versions of this paper were presented: *Intern. Symp. Macromol. Chem. Moscow, 1960*, II, 11 (1961); *Amer. Chem. Soc., Polymer Preprints*, 2 (2), 55 (1961).