in cyclohexylamine is found to be 16.25 (per hydrogen) (Table I), a value remarkably close to the aqueous pK. The $\mathrm{p}K_{\mathrm{CsCHA}}$ derives from ion pair equilibria involving various indicator hydrocarbons having delocalized carbanions and refers to an assigned "pK" of 18.49 for 9-phenylfluorene. This assignment is based on several measurements of 9-phenylfluorene in mixed aqueous organic solvents[17] using the H_- method; that is, subject to the usual approximations of the H_- procedure and their dependence on the indicator used, the pK of 18.49 assigned to 9-phenylfluorene is that for the aqueous standard state. If the ion pair equilibria in cyclohexylamine correspond to ionic equilibria in water, the derived pK's for other hydrocarbons are also those for the aqueous standard state. In particular, the true aqueous pK of 9-phenylfluorene cannot differ much from the assigned value of 18.49. For other conjugated hydrocarbons having extensively delocalized carbanions, the approximate independence of relative pK's to solvent[18] suggests that the $\mathrm{p}K_{\mathrm{CsCHA}}$ values are actually reasonable measures of aqueous ionic pK's. The agreement of the current direct comparison of cyclopentadiene in water and in cyclohexylamine confirms this view. That is, a series of assumptions and approximations comes full circle with satisfactory agreement. This argument applies, of course, only to those carbanions in which the anionic charge is sufficiently delocalized to avoid specific ion pair interaction effects.

Finally, we note that the current experimental determinations are close to previously assigned aqueous pK values. No significant changes in past applications and correlations involving cyclopentadiene are required, but these past applications are now given a sound experimental base.

References and Notes

(1) This series is a continuation of our series "Acidity of Hydrocarbons". The series name has been changed to reflect the actual scope of this research. For the paper considered LI in this series, see A. Streitwieser, Jr., and S. P. Ewing, *J. Am. Chem. Soc.*, **97**, 190 (1975).

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Organic Transition States. V. The Diels–Alder Reaction[1]

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Abstract: Ab initio molecular orbital theory has been applied to the study of the Diels-Alder condensation of ethylene and 1,3-butadiene. We find the reaction to proceed preferentially in a concerted manner via a symmetric transition state. Two-step pathways linking reactants and products are found to be higher in energy. Although our calculations suggest that the hex-2-ene-1,6-diyl diradical is locked in a set of conformational niches considerably below the energy of the concerted transition state, they by no means indicate its participation as an intermediate at the top of least activation pathway. Rather its only connection to the reaction is a transition state some 2 kcal/mol higher than the concerted.

Introduction

The Diels–Alder reaction is central to the history of organic chemistry.[7-11] Of major interest has been the deduction from recent experiments of the energy profile of the reaction,[12,13] a full knowledge of which is necessary to perfect our present understanding of the stereochemistry[7b,10,14,15] at both diene and dienophile, the endo-exo ratio,[7b,16,17] the regioselectivity,[8,11e,17d,18,19] the influence of donor- or acceptor-like substituents on the reaction rate,[7c,11d,20,21] the influence of catalysts[22,23] such as Lewis acids, and other effects such as the influence of pressure[24] and the "syn-anti" effect.[25]

Because of the relatively large number of atoms involved, only a few quantum-mechanical attempts have been made to evaluate the energy profile, even on the barest of all Diels–Alder reactions, the addition of ethylene to 1,3-butadiene. Historically, the earliest of such attempts, reviewed by Streitwieser,[26] employed Hückel molecular orbital calculations and were directed at relating the electronic properties of the diene to its reactivity. A second wave of calculations[17,19,21,23] used perturbation theory on a limited number of molecular orbitals, or even only the HOMO and LUMO frontier orbitals, to calculate numerically the relative π-stabilization energies of Diels–Alder transition states.

The first *all-valence electron* calculation is due to Kikuchi.[27] He restricted himself to the perfectly concerted symmetric process in which both new σ bonds are formed at the same rate. Unfortunately, although Kikuchi found an interesting electron transfer from 1,3-butadiene to ethylene in the incipient phase of the reaction, he discovered no energy maxima corresponding to transition states in the total ener-

Table I. Comparison of Experimental and Theoretical Energy Differences between Products and Reactants in the Diels-Alder Reaction[36]

	Experimental (kcal/mol)		Calculated (au)	
	$\Delta H_f°$ (0)	Zero-point energy	4-31G	4-31G + 3 × 3 CI
Ethylene (I)	14.52	30.89	−77.9212	−77.9212 (no CI)
1,3-Butadiene (II)	29.78	51.46	−154.6932	−154.7037 (3 × 3 CI)
Cyclohexene (III)	5.76	88.53	−232.6692	−232.6843 (3 × 3 CI)
(I + II) − III	38.54	−6.18 32.36 kcal/mol	0.0548 34.4 kcal/ mol	0.0594 37.3 kcal/mol

gy curves. The author ascribed this failure to the nature of the CNDO/2 method.

Recently, Dewar, Griffin, and Kirschner published a short account of their MINDO/3 calculation of the ethylene-butadiene reaction.[28] Their results indicate "that the transition state is very unsymmetrical, one new CC σ bond having been almost completely formed while the other has hardly begun to form at all".[11] They conclude that the reaction "cannot properly be classed as [a] concerted pericyclic process", but is a "two-stage" reaction.[8] We shall see that our conclusions are at variance with theirs.

Method of Calculation

The method of calculation is similar to that used in previous papers of this series.[1,29] The general philosophy consists of (a) scanning typical pathways with a *minimal basis set;* (b) optimizing the geometries of the extrema (transition states, reactants, and products) at this level; (c) recomputing the energy pathways, through the previously optimized geometries, with an extended basis set. The numbers in this paper correspond to stages b and c. We have used the GAUSSIAN 70 series of computer programs[30] and employed the minimal STO-3G[31] and extended 4-31G[32] basis sets.

Two calculations were performed concurrently, as in previous work.[1,29] First a "closed-shell" calculation using the classical Hartree-Fock operator for a closed-shell configuration

$$F = h + \sum_{j<a} (2J_j - K_j) + (2J_a - K_a) \qquad (1)$$

where the usual notation is employed and where the highest doubly occupied and west unoccupied orbitals are labeled, respectively, a and b. The companion "open-shell" calculation uses the single restricted open-shell Hamiltonian suggested by Nesbet[33]

$$F = h + \sum_{j<a} (2J_j - K_j) + (J_a - \tfrac{1}{2}K_a) + (J_b - \tfrac{1}{2}K_b) \qquad (2)$$

in which both orbitals a and b are assumed to be singly occupied.

A simple SCF calculation with either Hamiltonian, with the direct computation of the diagonal energies of the singlet configuration $^1a^2$ or ^1ab, is inappropriate for describing loosely bound transition states or diradicals.[34] The high-energy ionic terms in the molecular orbital description of a singlet diradical can be eliminated only via a 3 × 3 configuration-interaction treatment.[34] The three configurations to be mixed are $^1a^2$, ^1ab, and $^1b^2$. *It should be emphasized that a 2 × 2 CI treatment*[35] *restricted to* $^1a^2$ *and* $^1b^2$, such as used by Dewar,[28] will not eliminate the ionic terms unless a symmetry element in the calculated geometry forbids configuration ^1ab from mixing with the other configurations.

During the minimal basis set scan, we recalculated several geometries using a 15 × 15 CI procedure (detailed earlier by one of us[1a]). This study was prompted by the near degeneracy between the two highest doubly occupied orbitals in the concerted transition state structure (see text further). No significant change was observed in relative energies of different points, and the use of the 15 × 15 CI procedure was discontinued. Therefore, the 3 × 3 CI procedure is used coherently throughout the entire potential energy surface. In this manner, only the most labile pair of electrons is correlated throughout.

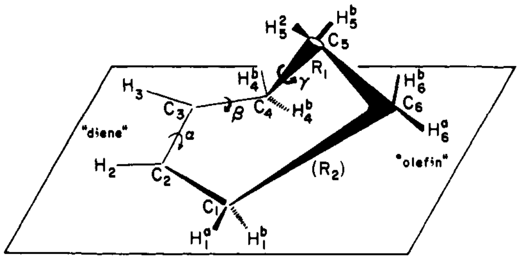


Figure 1. General coordinate system for the Diels-Alder reaction.

Results and Discussion

Thermochemical Comparisons. Our first concern is a comparison of the calculated and experimental energy differences between product, cyclohexene, and reactant, ethylene and 1,3-butadiene, molecules. The experimental data together with our theoreticaresults are presented in Table I. The former has been obtained by correcting the difference in enthalpies of cyclohexene and reactants at 0°K for the effects of zero-point vibrations (calculated as $\frac{1}{2}h \sum \nu_i$, where ν_i are the experimental vibrational frequencies). This leads to an enthalpy difference (products-reactants) of 32.36 kcal/mol. The 4-31G calculations alone yield an energy difference of 34.4 kcal/mol, which is increased slightly to 37.3 kcal/mol after the SCF energies of cyclohexene and 1,3-butadiene are corrected for the effects of valence shell correlation by use of the 3 × 3 CI procedure.[37,38] The geometries we have employed are detailed in the following section.

Optimized Geometries of Reactant and Product Molecules. The geometries of ethylene and *cis*-1,3-butadiene were optimized at the STO-3G level subject to the constraint that all CH bond lengths were held at 1.09 Å. The geometrical parameters are: (ethylene) $C{=}C$ = 1.306 Å, $\angle HCH$ = 115.6°; (*cis*-1,3 butadiene)[39] $C_1{=}C_2$ = 1.326 Å, $C_2{-}C_3$ = 1.470 Å, $\angle C_1C_2C_3$ = 126.6°, $\angle H_{in}C_1C_2$ = 121.5°, $\angle H_{out}C_1C_2$ = 122.8°, $\angle HC_2C_3$ = 114.9°.

For all other points on the surface, including cyclohexene, a general coordinate system was developed with enough flexibility to generate all the important intermediate geometries, including the multiple conformations of the hex-2-ene-1,6-diyl diradical. This general coordinate system was established in the following manner. Out of the 42 independent degrees of freedom, 17 were frozen throughout the search (Figure 1) [the ten CH bond lengths, fixed at

Table II. Geometrical Coordinates of Various Structures on the Diels-Alder Surface[a]

Energy, au	Cyclohexene	C	T_a'	(T_b')	T_a	(T_b)	D_a	(D_b)	R
(4-31G + 3 × 3 CI)	−232.6843	−232.5570	−232.5588	(−232.5588)	−232.5504	(−232.5516)	−232.5676	(−232.5651)	−232.5540
α	0.0	0.0	0.0		0.0		0.0		0.0
β	43.0	58.1*	98.2		90.0		90.0		68.7
γ	319.2*	309.6*	180.0	(300.0)	180.0	(300.0)	180.0	(300.0)	306.4
R_1	1.54	2.21	2.10		1.96		1.55		1.99
R_2	1.54	2.21	4.93	(3.64)	4.91	(3.53)	4.81	(3.19)	2.56
C_2C_3	1.35*	1.36*	1.46		1.45		1.39		1.37
C_1C_2	1.53*	1.40*	1.33		1.34		1.36		1.38
C_3C_4	1.53*	1.40*	1.37		1.41		1.43		1.44
C_5C_6	1.56*	1.40*	1.35		1.40		1.53		1.47
$C_1C_2C_3$	119.6*	120.4*	124.1		124.1		124.1		121.7
$C_2C_3C_4$	119.6*	120.4*	123.8		123.8		123.8		121.5
$C_3C_4C_5$	110.8*	104.8*	112.8		112.8		112.8		107.5
$C_4C_5C_6$	114.8*	108.2*	111.9		111.9		111.9		109.4
$H_2C_2C_3$	121.7*	120.3*	117.9		117.9		117.9		119.5
$H_3C_3C_2$	121.7*	120.3*	118.1		118.1		118.1		119.6
$H_4{}^aC_4H_4{}^b$	107.6*	113.8*	110.0		109.5		109.5		111.2
$H_4{}^aC_4C_3$	107.6*	119.4*			117.2		109.5		117.1
$H_4{}^aC_4C_3C_2$	78.2*	35.9*	19.5		23.7		32.1		35.3
$H_1{}^aC_1H_1{}^b$	107.6*	113.8*	120.0		120.0		120.0		115.8
$H_1{}^aC_1C_2$	107.6*	119.4*	120.0		120.0		120.0		119.4
$H_1{}^aC_1C_2C_3$	78.2*	35.9*	0.0		0.0		0.0		23.9
$H_6{}^aC_6H_6{}^b$	106.4*	114.9*	120.0		120.0		120.0		118.3
$H_6{}^aC_6C_5$	198.4*	119.1*	120.0		120.0		120.0		119.2
$H_6{}^aC_6C_5C_4$	57.6*	74.7*	90.0		90.0		90.0		79.8
$H_5{}^aC_5H_5{}^b$	106.4*	114.9*	110.0		109.5		109.5		112.2
$H_5{}^aC_5C_6$	108.4*	119.1*	119.2		117.2		109.5		117.0
$H_5{}^aC_5C_6C_4$	57.6*	74.7	69.7		66.4		58.4		68.7

[a] Variables which have been optimized for each geometry are marked with a star. Bond lengths are in angströms and angles in degrees.

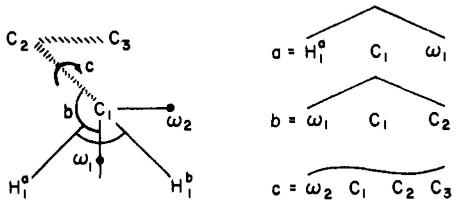


Figure 2. Coordinate system on a methylene group. The dihedral angle C is defined with respect to ω_2, so as to obviate for cases where ω_1 is colinear with C_1-C_2.

1.09 Å; the three dihedral angles, $\alpha = C_4C_3C_2C_1 = 0°$, $H_2C_2C_3C_4 = 180°$, $H_3C_3C_2C_1 = 180°$ (cis conformation) or $\alpha = C_4C_3C_2C_1 = 180°$, $H_2C_2C_3C_4 = 0°$, $H_3C_3C_2C_1 = 0°$ (trans conformation)], so that the "dienic" moiety is always coplanar: the four angles $\angle H_1{}^aC_1C_2 = \angle H_1{}^bC_1C_2$; $\angle H_4{}^aC_4C_3 = \angle H_4{}^bC_4C_3$; $\angle H_5{}^aC_5C_6 = \angle H_5{}^bC_5C_6$; $\angle H_6{}^aC_6C_5 = \angle H_6{}^bC_6C_5$ (i.e., the dienic CH_2 groups are assumed to be symmetric relative to C_1C_2 and C_4C_3, respectively; while the olefinic CH_2 groups are symmetric with respect to C_5C_6.

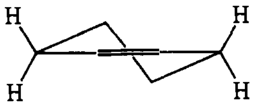
The remaining 25 coordinates were chosen as variables, although for certain pathways and geometries some of them were appropriately fixed. These 25 coordinates are: the five carbon-carbon bond lengths C_1C_2, C_2C_3, C_3C_4, C_4C_5, and C_5C_6; the two dihedral angles $\beta = C_2C_3C_4C_5$ and $\gamma = C_3C_4C_5C_6$; the four angles $C_1C_2C_3$, $C_2C_3C_4$, $C_3C_4C_5$, and $C_4C_5C_6$; the two angles $H_2C_2C_3$ and $H_3C_3C_2$, which completely determine the position of the in-plane methine hydrogens; for each methylene group, a set of three variables which determine the angles, say $\angle H_1{}^aC_1C_2$, $\angle H_1{}^aC_1H_1{}^b$, and $\angle H_1{}^aC_1C_2C_3$. In practice, two dummy atoms are introduced on each methylene group and the three independent variables *a*, *b*, and *c* are defined with respect to the position of these dummy atoms (Figure 2).

Returning to Figure 1 we must distinguish between two cases. The more general case is that where ethylene approaches the butadiene in an unsymmetrical manner. The most important variables along reaction paths of this type are the dihedral angles β and γ and the bond length R_1. The distance R_1 is assumed to correspond to the *shorter* of the two bonds which are forming during the reaction. The distance R_2, which represents the longer of the two bonds, is a complicated function of all the other internal coordinates. However, its numerical value depends essentially on the three variables β, γ, and R_1, and it will be calculated concurrently with these three quantities. A more specific case ($R_1 = R_2 = R_0$) corresponds to the perfectly concerted pathway. We consider this common distance as the primary variable. Symmetry then reduces the maximum number of total variables to 16 (R_0, C_2C_3, C_5C_6, β, γ, $\angle C_3C_4C_5$, $\angle C_4C_5C_6$, and one-half of the remaining previous 18 variables).

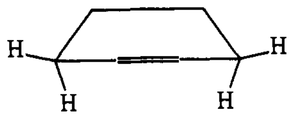
We have tabulated all 25 variables, plus α and R_2 for the important geometrical structures on the surface. These geometries, which should be helpful for future work on this problem, are shown in Table II, to which we will refer throughout this paper.

The first geometry of interest is that of cyclohexene itself. With the minimal basis set we have optimized the half-boat conformation keeping C_s symmetry. The distance $C_4C_5 = C_1C_6$ is found equal to 1.54 Å, while the olefinic bond is calculated to be 1.35 Å for an assumed C_5C_6 bond length of 1.56 Å. A comparison was also made, at the STO-3G level and without the use of the CI procedure, with the half-chair and quasi-copolanar (five in-plane carbon atoms) conformations. The relative energies are: half-chair, 0 kcal/mol; quasi-copolanar, 1.44 kcal/mol; half-boat, 5.12 kcal/mol. These results agree with the calculations of Bucourt and Hainaut,[40a] who obtained an energy of 6.93 kcal/mol for the difference between the half-boat and half-chair conformations, without an intermediate maximum. Anet and Haq deduced[40b] a difference of only 2.7 kcal/mol, but with an intermediate maximum of 5.3 kcal/mol. Allinger and coworkers calculated[40c] a difference of 4.3 kcal/mol with an intermediate maximum of 5.9 kcal/mol.

As an aside, the observation that the boat form of cyclohexene represents an energy maximum, rather than an intermediate local minimum, is not at all surprising in view of the known conformational preferences of acyclic alkenes. Thus, in the half-chair arrangement the orientation of the vinylic methylene groups (those immediately adjacent to the carbon-carbon double bond) is such that one linkage approximately eclipses the double bond, akin to the situation found in, say, propene in its equilibrium conformation.[41,42] On the other hand, twisting the ring into a boat geometry results in these same methylene positions staggering the double bond, which, if we again draw parallels to propene, is the arrangement of maximum energy on the rotational potential.



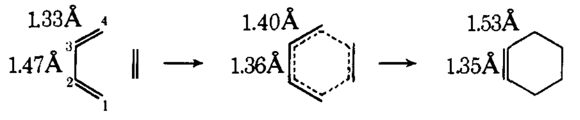
half-chair



half-boat

Concerted Pathway and Pure Two-Step Pathway. The first reaction coordinate to be investigated was the symmetric fully concerted pathway I with $R_1 = R_2 = R_0$. At regular intervals of this primary variable, the other degrees of freedom were optimized. Not surprisingly, the energy rises as the two reactants come together, reaches a maximum for a structure C, the *concerted transition state*, and then decreases monotonically as the system reaches cyclohexene.

The geometry of the concerted transition state C is shown in Table II. The internuclear distance R_0 is 2.21 Å, corresponding to relatively weak bond formation or, conversely, to remarkably stretched single bonds of the cyclohexene product.[43] The C_5C_6 bond is optimized at 1.41 Å, still relatively close to an olefinic double bond while, curiously enough, the dienic moiety is entirely destroyed with terminal bonds (1.40 Å) already longer than the central bond (1.36 Å). This indicates strongly, at the outset, that the *rearrangement of the butadiene skeleton* occurs at a very early stage of the reaction.



The $C_1C_2C_3$ fragment resembles its geometry in product cyclohexene far more than that in reactant butadiene. For a relatively exothermic reaction ($\Delta H = -32$ kcal/mol), the resemblance between transition state and product is somewhat in contradiction to Hammond's principle.[44] It is true, however, that the long C_1C_6 and C_3C_5 bonds (2.21 Å) are more akin to the situation in the reactants (no bonds) than in the product (1.50 Å).

A concerted pathway using half-chair conformations of the cycloadduct was also investigated. The energies of the half-chair transition states were much higher (~50 kcal/mol) than the previous half-boat transition state C.

Before considering the two-step pathway, let us investigate the geometry of the hex-2 ene-1,6-diyl diradical (D).

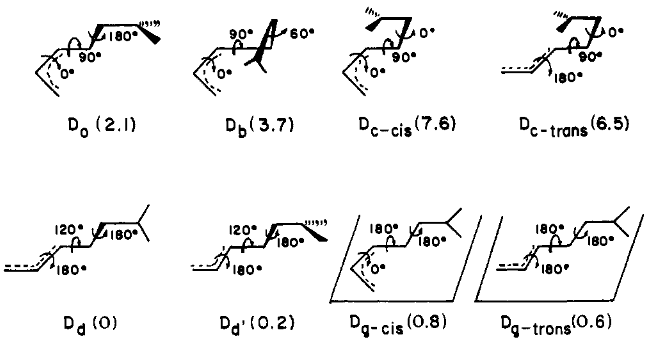
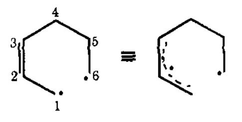


Figure 3. Conformations of the hex-2-ene-1,6-diyl diradical. Numbers in parentheses are energies (kcal/mol) above that of the ground-state form D_d.



D

The geometry of this diradical D was first optimized for the fully extended all-trans structure ($\alpha = 180°$, $\beta = 180°$, $\gamma = 180°$). After that, other conformations were explored by varying α, β, and γ. The set of conformations which we calculated are depicted in Figure 3, together with the values of α, β, and γ and their energies relative to the lowest one. The most interesting features of these structures are: the bond lengths in the allylic fragment ($C_1C_2 = 1.39$ Å, $C_2C_3 = 1.36$ Å); the distance $R_1 = 1.55$ Å; the distance R_2 between the radical sites on C_1 and C_6 which varies from a "minimum" of 3.19 Å in D_b to "maximum" of 6.33 Å in $D_{g\text{-trans}}$. The four first conformations a, b, c-cis, and c-trans are all "perpendicular" conformations ($\beta = 90°$) with the $C_4C_5C_6$ plane perpendicular to the $C_1C_2C_3C_4$ plane. Whereas the D_c structures are obvious candidates as starting points for a pathway between diradical D and vinylcyclobutane, structures D_a and D_b should be primordial diradical geometries on a pure two-step pathway.

We now consider the pure two-step pathway defined as first linking reactants to the relatively extended conformer D_a, next D_a to D_b via internal rotation, followed ultimately by a path from D_b to cyclohexene:

Two-step:

$$\text{reactants} \xrightarrow{(R)} D_a \longrightarrow D_b \xrightarrow{(R_2)} \text{cyclohexene}$$

The small $D_a \rightarrow D_b$ step, a rotation around the C_4C_5 bond ($\gamma = 180° \rightarrow \gamma = 300°$), has a small barrier ($\gamma = 240°$) of 4.0 kcal/mol. The final stage from D_b to cyclohexene has no activation energy. The formation of the first bond R_1, however, entails an energy maximum which occurs for a geometry T_a' shown in Table II. In this path, and for T_a' itself, only the bond lengths C_3C_4 and C_5C_6 adjacent to R_1 were optimized. The other parameters were obtained by linear interpolation between the optimized geometry D_a and the optimized geometries of ethylene plus butadiene.

The geometry of T_a' resembles that of D_a except for R_1, which has been stretched to 2.10 Å from 1.55 Å. In the minimal basis set framework, T_a' lies 35.4 kcal/mol above the diradical D_a. Although the energies of the STO-3G basis are clearly suspect,[38,43] this result is already a strong indication that the hex-2-ene-1,6-diyl diradical is not a maximum and not the transition state on the two-step pathway. It appears already that the diradical must lie *beyond* the two-step transition state, well on the side of the slope

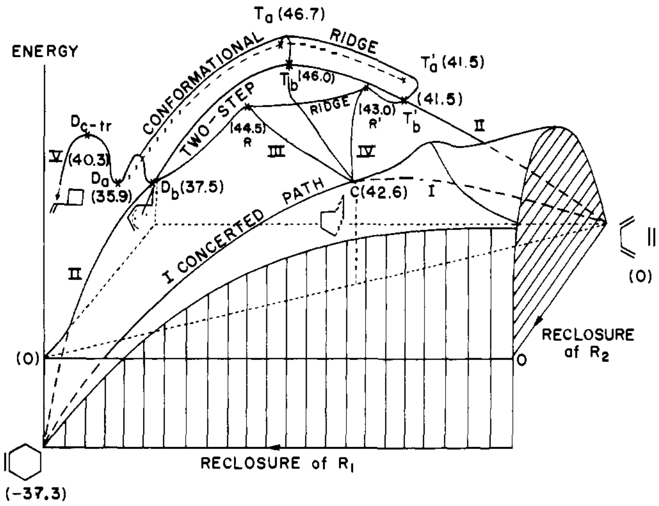


Figure 4. Energy profile for the Diels-Alder reaction: (- - -) hidden coordinate axes; (– – –) hidden pathways.

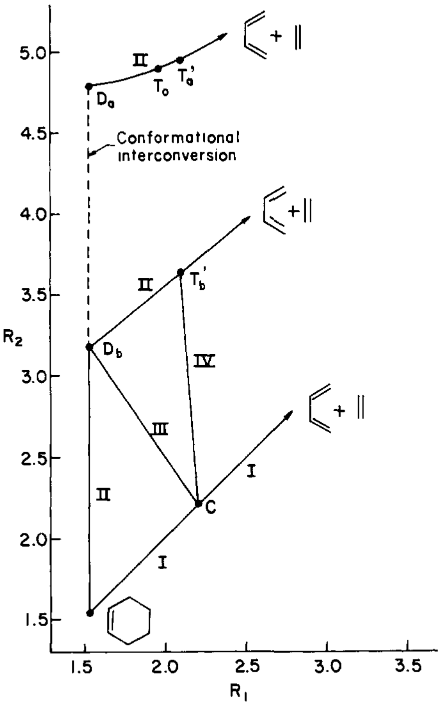


Figure 5. Positions (in R_1 vs. R_2 space) of important structures in the Diels-Alder mechanism and major pathways interconnecting them.

leading down to cyclohexene. We call T_a' *provisional two-step transition state;* further energetics (next section) displace the position of the maximum on the pure two-step profile.

A final rotation around C_4C_5 from T_a' leads, over a 1.1-kcal/mol barrier, to the conformer T_b' (γ = 300°), which could also have been obtained directly by stretching bond R_1 in D_b. T_b' and T_a' are interrelated in a similar fashion to D_b and D_a.

Pathways and Profiles. Energetics and Novel Features. As explained in the introduction, we proceed next to run the two previous paths

$$\text{reactants} \rightarrow \text{C} \rightarrow \text{cyclohexene} \qquad \text{(concerted)} \qquad \text{(I)}$$

$$\text{reactants} \rightarrow D_a \rightarrow D_b \rightarrow \text{cyclohexene} \qquad \text{(two-step)} \qquad \text{(II)}$$

with the energetically more reliable split-valence-shell 4-31G set. The results, which we will now examine, are

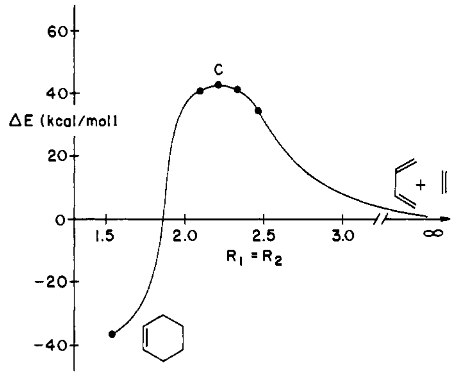


Figure 6. Concerted pathway to Diels-Alder reaction.

summarized in Figures 4–6. Figure 4 gives an overall three-dimensional representation of the entire potential surface. The positions (in R_1 vs. R_2 space) of the important points, as well as the major pathways connecting them, are displayed in Figure 5. Finally, a two-dimensional (energy vs. reaction coordinate) cut for the concerted pathway is presented in Figure 6.

The new calculation of the concerted pathway I yielded no surprise. The maximum still occurs for geometry C, with an activation energy of 42.6 kcal/mol. The 4-31G energetics of the two-step pathway II, however, showed a maximum whose geometry is pushed toward slightly shorter R_1 bond lengths than the previous maximum T_a'. In the new two-step transition state T_a, R_1 is 1.96 Å instead of 2.10 Å in T_a'.[45] The remaining geometrical parameters of T_a are obtained by interpolation between those of T_a' and those of D_a. A conformer T_b (γ = 300°), analogous to T_a, lies on the top of the pathway from T_b' to D_b.

The pure two-step transition state T_a lies at 46.7 kcal/mol above ethylene plus butadiene and, thus, *4.1 kcal/mol above the concerted transition state C.* The *diradical* D_a lies 10.8 kcal/mol below this two-step transition state, *well on the side of the descent from T_a to cyclohexene* and even 6.7 kcal/mol below the concerted transition state. These results seemed most encouraging to us, since they reconcile, for the first time, apparently contradictory experimental facts: the concerted nature of the reaction;[10] the low thermochemical energy of the hex-2-ene-1,6-diyl system, estimated by Benson[46] *to lie no higher than the transition state for the cycloaddition.*

However, the consistency of our results with experiment required exploration of a pathway from C, the concerted transition state, to D_b and D_a. A monotonically descending path would imply that D_a can be reached via C with no further activation and would contradict the experimental, quasiexclusive preference for a concerted pathway.

We therefore explored the pathways:

$$\text{C} \rightarrow D_b \qquad \text{(III)}$$

$$\text{C} \rightarrow T_b' \qquad \text{(IV)}$$

Intermediate geometries on these paths were chosen via the usual linear interpolation techniques. On each of these pathways a new maximum was found, R on path III and R′ on path IV. *The new col R serves as a barrier forbidding molecules in the concerted transition structure from freely rearranging to diradical.* Its energy, 44.5 kcal/mol above reactants, is 1.9 kcal/mol above C. On the energetic profile there now appears, adjacent to the concerted pathway C, a ridge defined by

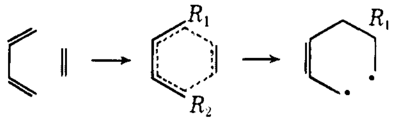
$$\text{reactants} \rightarrow \text{R}' \rightarrow \text{R} \rightarrow \text{cyclohexene}$$

which separates species forming concertedly from those forming in a two-step manner.

The novel, exciting feature constituted by the ridge RR′ resolves the apparent contradiction between kinetic and stereochemical results on the one hand and thermochemical results on the other. However, it automatically raises new questions. By revealing a barrier of only 44.5 kcal/mol on the composite path:

$$\text{reactants} \xrightarrow{\text{(I)}} \text{C} \xrightarrow{\text{(III)}} \text{R} \xrightarrow{\text{(III)}} \text{D}_b \xrightarrow{\text{(II)}} \text{cyclohexene}$$

the calculation implies that the most favorable pathways to diradical D are not pure two-step pathways. The best way to reach the diradical is through a *partially concerted* pathway starting out with nearly equal formation of both bonds (as along the ridge) and then continuing by a rearrangement which shortens one bond further while lengthening the other bond anew.



Energywise, the better two-step pathway through R lies no more than 1.9 kcal/mol above the best concerted pathway. This difference is somewhat smaller than indicated[47] by Bartlett's experiments with rate constants in the ratio of 5000 to 1 (~7.6 kcal/mol at 450 K) for the concerted (to cyclohexene) and "diradical" (to vinylcyclobutane) mechanisms of cycloaddition of ethylene and butadiene, although the agreement would be excellent with calculated pathways through T_b. We first explored the possibility that this discrepancy was due to another col, higher than R, lying between D_a and vinylcyclobutane. Such a pathway:

$$\text{D}_a \rightarrow \text{D}_{\text{c-cis or -trans}} \rightarrow \text{vinylcyclobutane} \qquad \text{(V)}$$

showed its highest energy near D_c, around 41–43 kcal/mol, i.e., below R. Another possibility is that two-step pathways through R involve a small additional *dynamic* barrier. Indeed the sudden switch, in the process:

$$\text{reactants} \rightarrow \text{R} \rightarrow \text{D}$$

from a symmetric (R_1 decreasing, R_2 increasing) stretching mode to an antisymmetric (R_1 decreasing, R_2 increasing) stretching mode implies a sharp right angle for the trajectories in multidimensional space and must be dynamically costly.

The consequence of such a dynamic barrier might be to raise the effective activation energy of R to the level of T_a. The concerted pathway would then be favored by 4 kcal/mol, instead of ≈2 kcal/mol, in better agreement with the experiment.

To summarize, the optimum pathway for the Diels–Alder condensation of ethylene and 1,3-butadiene is found to be one which is symmetrical, concerted, and requiring an activation of 42.6 kcal/mol. The experimental activation energy is 34.3 kcal/mol.[48] To reach the hex-2-ene-1,6-diyl diradical, two alternative routes are possible: a partially concerted pathway, which runs parallel to the fully concerted route and then branches off as one bond shortens while the other lengthens; and a pure two-step pathway, in which a single bond forms continuously.

A Study of the Frontier Orbitals along the Major Pathways. Any study of substituent effects in the Diels–Alder reaction based on the previous results would require intimate knowledge of the electronic features of points such as C, R, and T_a. Crucial features are the amplitudes of the frontier molecular orbitals, which are most liable to be perturbed by substitution, particularly by donor or acceptor groups.

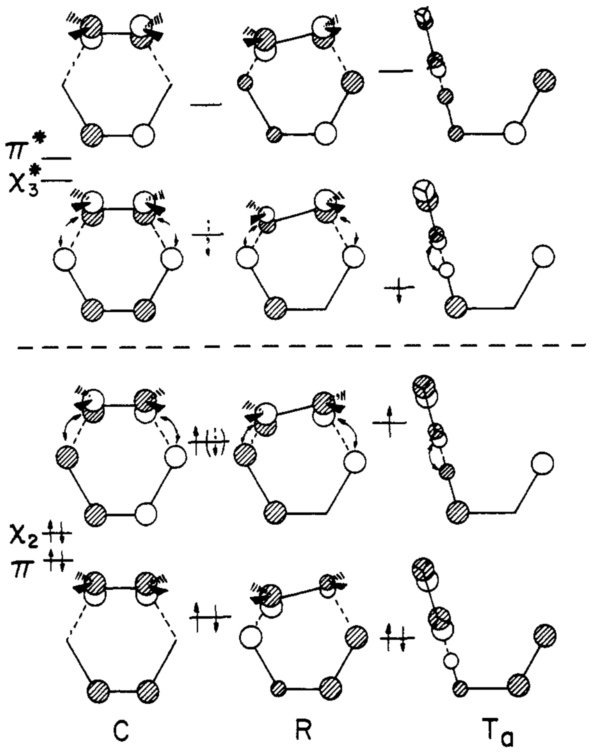


Figure 7. Frontier and near frontier molecular orbitals at the various cols of the Diels–Alder surface. Approximate orbital energies are also shown.

We compare the amplitudes of the two highest "occupied" and two lowest "unoccupied" orbitals of C, R, and T_a[49] (Figure 7).

In the concerted transition state C, the frontier occupied MO is *bonding* (full arrows) between the interacting termini, while the frontier empty orbital is *antibonding* (dotted arrows). The other two MO's are locally bonding (or antibonding), but essentially *nonbonding* between the termini of the reacting species. Considering next the ridge structure R, we see that the bonding character in the HOMO and the antibonding character in the LUMO is maintained along both R_1 and R_2. In T_a, however, in which only bond R_1 is partially formed, the HOMO is very weakly antibonding and the LUMO weakly bonding. However, since both orbitals are occupied on average by one electron, we do not attach too much significance to this effect.

The molecular orbitals of the concerted transition state C deserve further analysis. The lowest one, subjacent to the HOMO, is clearly derived from the olefin π orbital. Its form is identical with that described by Woodward and Hoffmann[50] and can be interpreted by the mixing of the lower butadiene π orbital χ_1 into the olefin π orbital in an *antibonding* manner and of the higher butadiene π^* orbital χ_3^* in a *bonding* way. The frontier HOMO is derived from the second butadiene π orbital χ_2, into which the higher π^* ethylene orbital has been mixed in a bonding manner. Similarly, the frontier LUMO is adequately described by the butadiene orbital χ_3^*, into which the lower olefin π orbital has been brought in as antibonding. Finally, the orbital superjacent to the LUMO is approximated by π^* (ethylene) mixed with some χ_1 (in bonding manner) and χ_2 (in antibonding manner), leaving little amplitude at the butadiene termini.

The ordering of the four orbital energy levels in C is characterized by the near degeneracy of the top two occu-

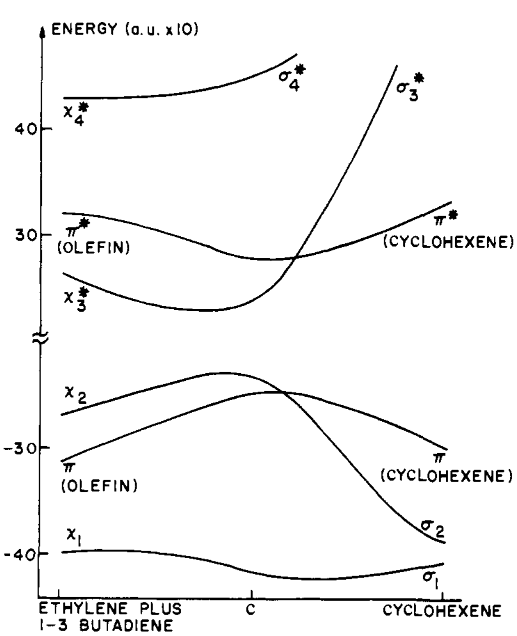
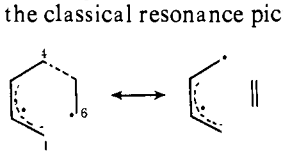


Figure 8. Orbital energies (minimal basis set) of the six "π" levels of reactants along the concerted pathway (I). The molecular orbital notation is that of Woodward and Hoffmann.[50] A similar figure was first obtained by Jorgensen.[51]

pied orbitals and by that of the lowest empty pair. This implies that, along the reaction coordinate described by the Woodward-Hoffmann correlation diagrams and which corresponds to pathway I, the transition state C occurs only slightly before the dienic orbital χ_2 intersects the olefinic π orbital. In the Woodward-Hoffmann diagram, χ_2 descends monotonically while π remains nearly equienergetic. Unpublished CNDO/2 calculations by Jorgensen indicate,[51] however, that the concerted transition state corresponds to a *maximum* in both π and χ_2 (and to a minimum in χ_3^* and π^*). The variation of the ab initio orbital energies of the six "π" levels of the reactants, shown in Figure 8, confirms this trend. Both Jorgensen's results and our own prove unambiguously that the qualitative correlations in the Woodward-Hoffmann diagram are correct, and that, even if several coordinates vary simultaneously, *orbitals of the same symmetry,* such as π and χ_1, *do not cross.* These results seem to lay at rest proposals to the contrary, such as made by Millie[52] and Nohira,[53] and to fully support Hosoya's contentions.[54]

Let us return now to the orbitals of the pure two-step transition state T_a. The "diradicaloid" nature of T_a appears clearly if we consider the sum and difference of the two frontier orbitals (Figure 9). One orbital is allylic nonbonding on carbons 1 and 3 (with a small admixture on 5), while the second is concentrated principally on the terminal carbon 6, but with some amplitude on carbon 4. These results are coherent with the classical resonance picture:



and with the short C_3-C_6 bond (1.39 Å) in T_a.

Studies of regioselectivity might usefully take advantage of the orbital aptitudes of R or T_a, *insofar* that the pathway in a regioselective reaction is *two-step.* Indeed, the stabilization of the two frontier orbitals may be different in the four transition states, leading to a preference for one over the others. Similarly, studies of donor or acceptor effects on reaction rates might be estimated from the destabilization or stabilization of the orbital energies of π and χ_2 of C, under the restriction that the real pathway is concerted.

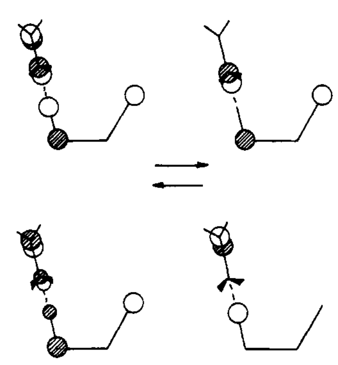
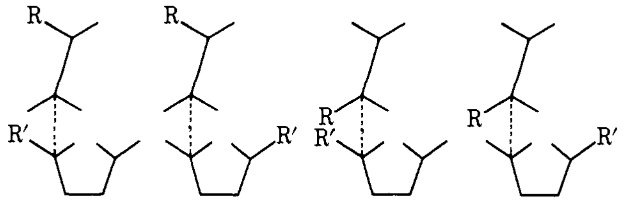


Figure 9. Delocalized and localized frontier orbitals of T_a.



Conclusion

Our main result is that the Diels-Alder condensation of ethylene and butadiene proceeds concertedly through a symmetric transition state. Furthermore, two distinct two-step pathways have been revealed: one in which a lone bond is formed without participation by the other nonbonded termini; and a second, lower pathway in which concertedness or quasi-concertedness (2.0 Å $< R_1, R_2 <$ 2.5 Å) is followed by violent antisymmetric bond rearrangement (to R_1 = 1.55 Å, R_2 = 4.8 Å).

The symmetric nature of the computed transition state **C** is in agreement with the most recent experimental measurements of secondary isotope effects for related Diels-Alder reactions.[55] It is not at variance with the famous Woodward-Katz "two-stage" hypothesis,[8] since the latter was proposed for the condensation of two dienes, for which, *on symmetry grounds alone,* R_1 and R_2 cannot be expected to be identical at the transition state. It contradicts, however, the recent MINDO/3 calculations by Dewar and coworkers.[28] The reason for the discrepancy of our results with Dewar's is not clear. If anything, and as mentioned earlier, inclusion here of 3 × 3 CI, rather than 2 × 2 CI, should favor unsymmetrical pathways over symmetrical ones (where symmetry reduces the configuration interaction matrix to 2 × 2). We have verified that our CI corrected results parallel those at the 4-31G level alone. For instance C, T_a', and R are found to have relative 4-31G energies 0, −0.6, and 8.6 kcal/mol, respectively, compared with values of 0, −1.1, and 1.9 kcal/mol after configuration interaction. One possibility is that we have not put quite as much effort into the geometrical optimization of T_a' (and hence T_a) as we have into C and D. Pathway II, thus, may be slightly too high. Yet, the other two-step transition geometry R, on a linear interpolation path between fully optimized C and fully optimized D, also lies above the concerted transition state C.

A second major result is that the hex-2-ene-1,6-diyl diradical lies well below the maximum on the two-step profile. The diradical appears here as a set of conformational niches on the far side of the hill formed by the two-step pathway. It is *not,* by any means, a secondary minimum at the top of any pathway. After a diradical transition state[29a] and a diradical secondary intermediate,[29b] quantum-mechanical calculations now reveal a diradical "*transient point*" on a hillside, some 7-10 kcal/mol below the various transition states. Furthermore, the best pathway to the diradical (through R) is only 2 kcal/mol more expensive than the concerted route. This raises the strong possibility[56] that many Diels-Alder reactions for substituted reactants actually *proceed through a diradical, even though this diradical is not observed.*

A third interesting conclusion follows from Figure 6. As first noted by Jorgensen,[51] the initial slopes of π, χ_2, χ_3^*, and π^* show that frontier HOMO-LUMO interactions[9,21] do *not* dominate the incipient stage of the Diels-Alder reaction. Frontier orbitals may discriminate between favorable and unfavorable reactions, but other energy terms are larger in size at the early stages. Closed-shell repulsions (mixing of filled orbitals) and orbital energy changes resulting from geometrical distorsion of addends[57] will be dominant here. Only in the region of the transition state will stabilizing HOMO-LUMO interactions overcome these destabilizing terms. Thus, frontier orbital interactions may still, in one sense, determine the energy and position of the transition state along the reaction coordinate, especially if the destabilizing terms are relatively constant for different types of Diels-Alder reactions. In any case, our calculations support Fukui's postulate that the frontier orbital energy gap first *narrows* before widening. It seems that a good part of the activation energy of the reaction can be traced to the energy increase of the filled olefinic π orbital, which is obliged to mix with the lowest filled butadiene χ_1 orbital in an antibonding manner. Interestingly enough, although it is true that the olefinic π orbital correlates with the cyclohexenic π orbital according to the *principle of conservation of orbital symmetry,* it is also true that Nature partakes sweet revenge by imposing a costly energy on this exhaustive electronic rearrangement.

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(38) The reader will appreciate the energetic unreliability of the minimum basis set in terms of the corresponding number given in STO-3G plus 3 × 3 CI: 109.9 kcal/mol. The reliability of this basis set for geometries, however, has been amply demonstrated; see W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974); W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).

(39) The *cis* conformation is not a stable equilibrium conformation of 1,3-butadiene; see R. L. Lipnick and E. W. Garbisch, *J. Am. Chem. Soc.*, **95**, 6370 (1973).

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(41) Experimental: D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.*, **28**, 728 (1958).

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(43) The minimal basis set activation energy is 36.8 kcal/mol, which is in better agreement with experiment (34.3 kcal/mol) than our final extended basis set value of 42.7 kcal/mol (see further). However, as already pointed out,[38] the thermochemical energies in the minimal basis calculation are extremely poor, putting cyclohexene 109.9 kcal/mol below reactants (experimental: 32.36 kcal/mol), and the diradical D only 1.3 kcal/mol above reactants.

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Kinetics of the Stereospecific Photochemical Cyclodimerization of 2-Butene in the Liquid Phase[1a]

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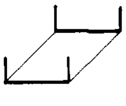
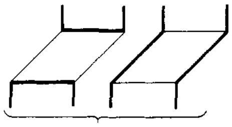
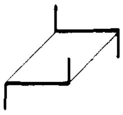
Abstract: Stereoselective photochemical cyclodimerization of liquid 2-butene, recently observed in this laboratory, has been investigated in greater detail. Particular attention has been paid to the kinetics of the cyclodimerization, which occurs with retention of geometric configuration in both 2-butene molecules incorporated into the cyclodimer. In mixtures of *trans-* and *cis*-2-butene, the distribution of the four isomers of the cyclodimer (1,2,3,4-tetramethylcyclobutane) undergoes characteristic drastic changes as the ratio of the two olefins is varied. The experimentally observed distribution of the four isomers as a function of the cis/trans ratio in the liquid 2-butene can be quantitatively reproduced by calculations based on theoretical rate expressions derived from a reaction mechanism which considers the statistical probability of encounters between the electronically excited and the ground-state *cis-* and *trans*-2-butene molecules. The effects of variation of the wavelength and the temperature on the extent of cyclodimerization in liquid 2-butene relative to its isomerization, acyclic dimerization, and photolytic fragmentation (followed by free radical reactions) have been investigated. At higher temperature and especially at shorter wavelengths, the extent of acyclic dimerization and photolysis tends to be enhanced. At 184.9 nm acyclic dimerization and photolytic processes predominate, and only relatively little cyclodimerization takes place. At 213.9 nm some cyclodimerization is observed even in the gas phase, especially at higher pressures, but its extent is very much smaller than in the liquid phase. No cyclodimerization is observed in the gas-phase triplet mercury, Hg $6(^3P_1)$, photosensitized reaction. Quantitative data have been obtained on the very rapid reduction in the extent of photochemical cyclodimerization of liquid 2-butene as a result of dilution with isopentane.

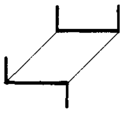
Introduction

In a previous communication[2] from this laboratory, it was reported briefly that photochemical cyclodimerization of liquid 2-butene takes place with retention of geometric configuration in both 2-butene molecules which become incorporated in the cyclodimer. This can be represented schematically by the structural diagrams of the four 1,2,3,4-tetramethylcyclobutane isomers formed, in which the original two 2-butene fragments are indicated by heavier lines.


A
(cis,cis,cis)


B
(cis, trans, cis)


C
(trans,trans,trans)


D
(cis,cis,trans)

It is evident that if the cyclodimerization is to occur with complete retention of configuration, pure *cis*-2-butene would have to form only A and B, pure *trans*-2-butene only B and C, while the remaining isomer D could be formed only in mixtures of *cis-* and *trans*-2-butene (in addition to A, B, and C). Such a remarkable selective formation of the four isomers is actually observed.[2]

Photochemical cyclodimerizations leading to the formation of cyclobutane ring compounds are frequently observed. They have received much attention in organic photochemistry,[3-5] more recently from the point of view of conservation of orbital symmetry, as well as in photobiology.[6-8] Photochemical cyclodimerization of liquid tetramethylethylene to octamethylcyclobutane has also been recently reported,[9,10] although it is, of course, not possible in this case to establish whether or not the process occurs with retention of configuration. Observation of complete retention of configuration in the photochemical cyclodimerization of liquid 2-butene provides, therefore, new insight into the mechanism of some of these photochemical processes. Moreover, studies of photochemical cyclodimerization to cyclobutane