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The Resonance Energy of Transition States. The Cyclobutene–Butadiene Energy Surface

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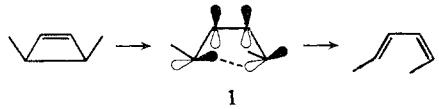
In this Account we discuss some recent work from these and other laboratories directed to the question: what is the energy advantage associated with a reaction which is orbital symmetry allowed[1] as opposed to a forbidden or noninteracting pathway? We use the cyclobutene–butadiene transformation to illustrate the methods and difficulties associated with making such a determination. Discussions and calculations on the reaction paths which link these valence isomers have dominated both the educational[2] and scientific[3] literature concerned with orbital symmetry control and make the cyclobutene–butadiene surface an attractive candidate for a complete study.

The concept that the sense of the connectivity of interacting orbitals can influence stability of chemical species can now be seen to occupy an extremely important position in organic chemistry. Hückel developed this idea by showing that the *number* of interacting π orbitals in a cyclic array dramatically influences stability. This finding, which is recognized as one of the triumphs of simple molecular orbital theory, is embodied in the Hückel $4n + 2$ rule. This rule has been enormously successful and has led to many developments in both synthetic and theoretical chemistry.[4]

The papers of Woodward and Hoffmann in the middle 1960's extended this reasoning to transition-state species. This powerful insight, which had a profound impact on organic chemistry, was originally described in terms of classical orbital and state correlation diagrams. However, it is often convenient for many purposes to view the Woodward–Hoffmann rules as transition-state analogs of the ground-state $4n + 2$ Hückel rule. The addition of the Möbius ring formalism completes this overall scheme.

Thus, transition-state assemblies with $4n$ mobile electrons are extraordinarily stable if the connectivity is cyclic in the Möbius sense (an odd number of sign inversions in the basis set). A collection of $4n + 2$ mobile electrons arranged in the Hückel cyclic sense (zero or an even number of sign inversions) shows comparable special stability.[3d] These ideas are easily illustrated for the cases of cyclobutene and cyclohexadiene. In each case an arbitrary basis set is drawn to represent the Möbius (1) or Hückel (2) nature of the cyclic array of transition-state basis orbitals.



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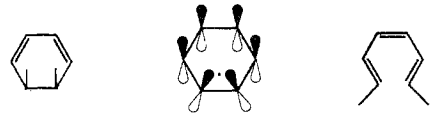

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(1) In this Account we make use of four terms in classifying reactions: (orbital symmetry) allowed, (orbital symmetry) forbidden, nonallowed, and noninteracting or diradical. In referring to reactions which could conceivably proceed by a cyclic transition state, the term *allowed* will be used to designate those transition states which obey either the Hückel or Möbius $4n + 2$ or $4n$ rules, or are otherwise clearly favored energetically relative to some noncyclic model. The term *forbidden* will be reserved for those reactions which follow a cyclic but energetically unfavorable pathway relative to the allowed route. The term *noninteracting* (or *diradical* where appropriate) will be reserved for reactions which can be clearly characterized as having no simple cyclic connectivity in the transition state even though such a cyclic pathway is conceivable. *Nonallowed* will be used in a general sense and can include both of the latter two terms. For present purposes "nonallowed" is a particularly useful way of describing a reaction for which the experimental situation allows no clear distinction between diradical and forbidden pathways to be made.

(2) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; (b) R. E. Lehr and A. P. Marchand, "Orbital Symmetry," Academic Press, New York, N. Y., 1972; (c) R. Breslow, "Organic Reaction Mechanisms," 2nd ed, W. A. Benjamin, New York, N. Y., 1969.

(3) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); (b) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (c) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (d) H. E. Zimmerman, *ibid.*, **4**, 272 (1971); (e) K. Fukui, *ibid.*, **4**, 57 (1971); (f) R. G. Pearson, *ibid.*, **4**, 152 (1971).

(4) For details of both experiment and theory see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

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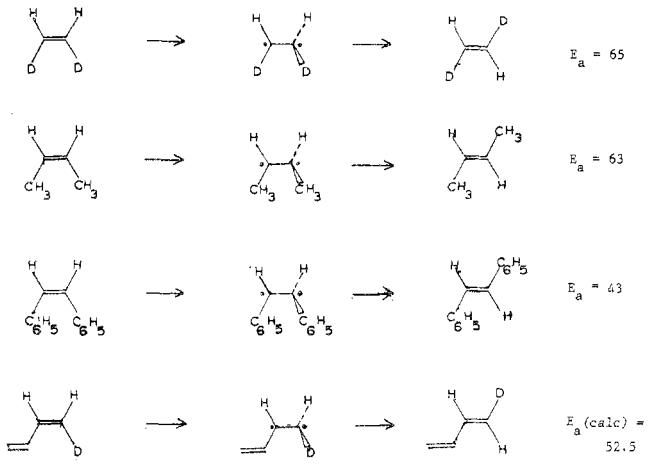


Figure 1. Activation energies for cis–trans isomerization (kcal/mol).

The qualitative nature of such arguments is in many ways one of the most appealing aspects of the orbital symmetry rules. Predictions can almost always be made without recourse to numerical analyses or calculations while still using methods easily related to sound theoretical arguments. Nevertheless, the magnitude of the stabilization due to these favorable interactions in the transition state is a point of considerable interest. On the simplest level, if stabilizing interactions are small (0–5 kcal/mol), detection of nonallowed products will be routine; if the empirical transition-state resonance energies are large (10–20 kcal/mol), detection of nonallowed products will be very difficult, and for practical purposes the reaction will be described as giving only allowed products. It seems unlikely that the interactions in the transition state for any cyclic reaction could be so well developed that the empirical resonance energy would match or exceed that of benzene, ~36 kcal/mol.

We now follow this introduction with four sections which illustrate several of the aspects to which we have alluded. First we demonstrate the need to consider orbital-symmetry-allowed pathways even in cases where exceedingly simple alternates are available. We then move to description of a system which allows the determination of a stabilization energy associated with an allowed pathway. This treatment is concluded with an analysis of a reaction which proceeds by an apparently nonallowed route, followed by brief comments on quantum based calculations of the cyclobutene–butadiene pathway.

Cis–Trans Isomerization in Butadiene. The cis–trans isomerization reactions of simple olefins and small-ring compounds have been analyzed and studied for many years,[5] doubtless due in part to the exceedingly simple mechanism imagined for this process. Interpretations involving 1,2-diradical-like transition states have been encouraged by the fact that substituents lowered the energy required for the reaction by about that amount expected from stabilization of the radical center, if ground-state strain factors are removed. This effect is illustrated by the first three entries in Figure 1. Thus the cis–trans isomerization reactions of butadiene (Figure 1) would be expected to proceed at a substantially lower temperature relative to that of ethylene because of the potential allylic resonance (12.5 kcal/mol using methylallyl radical as a model). We estimate[6] E_a = 52.5 kcal/mol for this diradical reaction (65.0 − 12.5 kcal/mol). This path is not obviously subject to orbital-symmetry control, since no simple cyclic connectivity of the π orbitals exists.

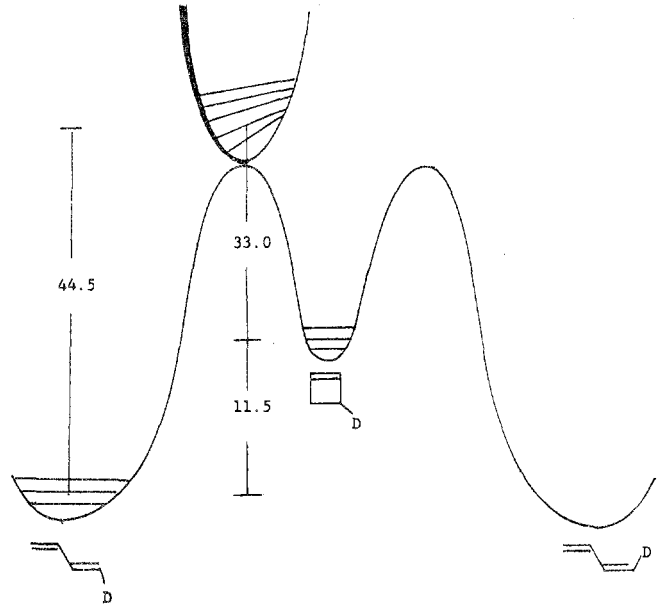
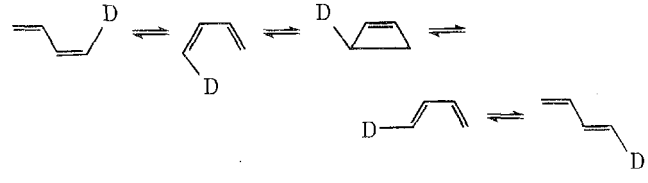


Figure 2. Energy relationships (kcal/mol) on the butadiene–cyclobutene surface.

An allowed pathway can be formulated which proceeds *via* the cyclobutene, however. Knowledge of all



the pertinent activation parameters and ground-state energy differences led us to propose[7a] that such a pathway would be important for butadiene. Our analysis[6,7a] of the cyclobutene isomerization pathway is shown in Figure 2 and predicts an activation energy of 44.5 kcal/mol, 8 kcal/mol lower than that estimated for the 1,2-diradical mechanism. Support for this contention had already appeared in the literature. In a highly substituted system Doorakian and Freedman[8] were able to implicate cyclobutene intermediates convincingly. Frey, Lamont, and Walsh[9] noted that activation parameters for the cis–trans isomerization of 2,3-dimethyl-1,3-pentadiene were somewhat lower than those required for the diradical pathway and suggested a cyclobutene intermediate. However, these systems do not allow the competition between diradical and cyclobutene pathways to be probed quantitatively, and we sought a simple sub-

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

(6) L. M. Stephenson, R. V. Gemmer, and J. I. Brauman, *J. Amer. Chem. Soc.*, 94, 8620 (1972).

(7) (a) J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, 94, 4262 (1972); (b) J. I. Brauman and W. C. Archie, Jr., *Tetrahedron*, 27, 1275 (1971).

(8) G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, 90, 5310, 6896 (1968).

(9) H. M. Frey, A. M. Lamont, and R. Walsh, *J. Chem. Soc. D.*, 1583 (1970).

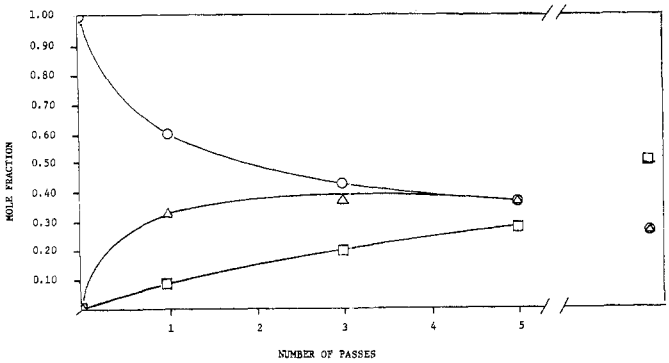
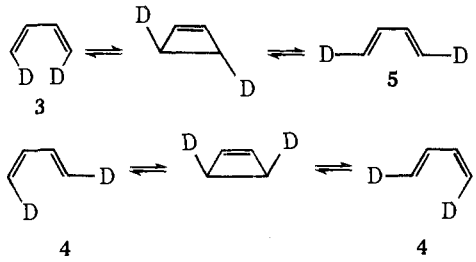


Figure 3. Pyrolysis of pure *cis,cis*-1,4-dideuterio-1,3-butadiene (○) to *trans,trans*-1,4-dideuterio-1,3-butadiene (△) and *cis,trans*-1,4-dideuterio-1,3-butadiene (□) at 910 K, at a pressure of 3 Torr; contact time per pass was ~50 msec. The points at the far right side of the graph represent the expected equilibrium values.

strate capable of revealing the several reactions simultaneously.

The cyclobutene path would be subject of course to the constraints of the Woodward-Hoffmann rules, which require, in this case, a correlation of the rotational motion of the two termini of the diene unit. Thus a disubstituted olefin would be expected to behave as pictured below, provided that the orbital symmetry rules are rigidly obeyed.



Because of the simplicity of the system, and because thermochemical data were available for butadiene and cyclobutene and could be accurately transferred to the deuterio dienes, we studied the thermal chemistry of dienes **3**, **4**, and **5**. The details of their preparation, involving as the crucial step the Zn (Cu) reduction of the corresponding chloro compounds in refluxing dioxane-D_2O, will be described elsewhere.[10]

Vacuum flash pyrolysis was employed to isomerize these dienes. Wall-catalyzed reactions are particularly important in this system, and the use of high temperature and short contact times (910 K for 50 msec at a pressure of ~3 Torr) minimized these effects. Figure 3 shows that pyrolysis of **3** (*cis,cis*-1,4-dideuteriobutadiene) leads to **5** (trans,trans) much more rapidly than to **4** (cis,trans). A similar set of results was obtained starting with **5** (trans,trans). These data require that starting with pure isomers the rates of disappearance of **3** (cis,cis) and **5** (trans,trans) would be much faster than the rate of disappearance of **4** (cis,trans). Independent determinations of disappearance rates show that $k(3 \rightarrow 5) \simeq k(5 \rightarrow 3) \simeq 10k(4 \rightarrow 3 + 5)$, in confirmation of this supposition.

These experiments are consistent with the intervention of cyclobutene in the double isomerization pathway. Since the heats and entropies of formation

(10) L. M. Stephenson and R. V. Gemmer, manuscript in preparation.

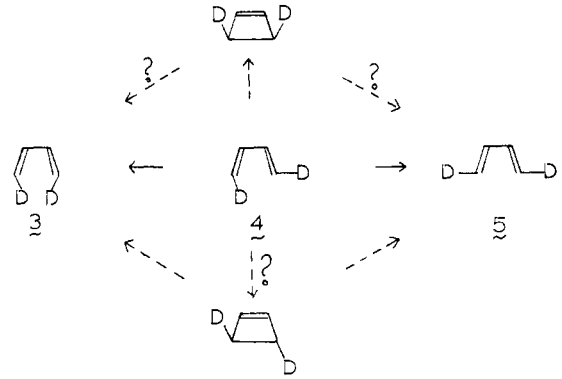
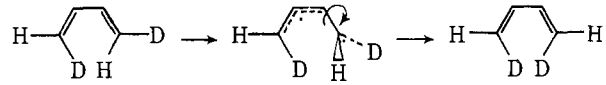


Figure 4. Possible origin of nonallowed products in butadiene isomerization.

of cyclobutene and butadiene are well known,[11a,b] and the activation parameters for the cyclobutene ring-opening reaction have been accurately measured,[11b,12] the rate of ring closure of the diene to cyclobutene and hence the rate of double isomerization are calculable; $\log k(3 \rightarrow 5) = 12.3 - 44.5/2.303RT$. Our measured rate constant for this reaction, $k_{obsd} \simeq 12\ sec^{-1}$, may be compared to the prediction of this equation, $k_{calcd} = 50\ sec^{-1}$ at 910 K.

Isomerization of **4** (cis,trans) to **3** (cis,cis) and **5** (trans,trans) cannot involve the correlated double isomerization. By taking into account the full allylic resonance energy[5] of species **6**, a 1,2-diradical pathway can be shown to describe this reaction adequately. Thus, we estimate $\log k(4 \rightarrow 3)$ or $k(4 \rightarrow 5) = 12.8 - 52.5/2.303RT$. Our measured rate constant for this reaction, $k'_{obsd} \simeq 0.6\ sec^{-1}$, compares favorably with $k'_{calcd} = 1.9\ sec^{-1}$ at 910 K.



4 **6** **3**

The agreement between the calculated and observed rates for both the double isomerization and 1,2-diradical pathways is within tolerable limits. In addition, at 3-Torr total pressure, the butadiene reactions have probably not yet reached the high-pressure limit, a factor which would lower the rates from the calculated values.

It is conceivable that the isomerization of the cis,trans diene to the cis,cis and trans,trans dienes (and the reverse reactions) involves a set of two electrocyclic reactions, one allowed and one forbidden (Figure 4). However, the reasonable agreement between the calculated diradical pathway rate and the rate of production of either **3** or **5** from **4** leads us to postulate that the diradical route is responsible for the nonallowed reaction. The forbidden electrocyclic ring-closure paths marked with question marks in the figure will be shown below to be even less favorable. Nonetheless, the diene isomerization experiments place a lower limit on the energy increment associated with the forbidden electrocyclic reaction as contrasted to the allowed pathway. If a forbidden reaction is involved in the isomerizations **3** ⇄ **4** ⇄ **5** (see

(11) (a) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968); (b) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 21** (1970).

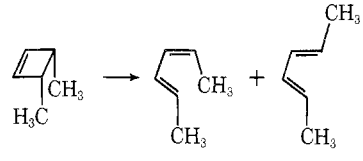
(12) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **69**, 1073 (1965).

Figure 4), then this energy difference is 8 kcal/mol. If, as we have suggested, a simple 1,2-diradical pathway is operating here, then this energy difference will be greater than 8 kcal/mol.

It is also clear from these results that all dienes sterically unencumbered in the 1 and 4 positions must isomerize *via* cyclobutene intermediates. In fact, steric crowding in the 2 and 3 positions should lead to an increased preference for cyclobutene so that substituted dienes should favor the electrocyclic pathway even more dramatically. This can be seen clearly in the work of Doorakian and Freedman,[8] who noted that *cis,trans*-2,3,4,5-tetraphenyl-2,4-hexadiene isomerized cleanly (*via* the cyclobutene only) even when heated for prolonged periods of time, during which time each molecule, on average, isomerized about 100 times.

Thus the experiments with the simple deuterated dienes and, in addition, the elegant work of Doorakian and Freedman noted above suggest a lower limit of ~8 kcal/mol for the resonance energy of the aromatic transition state. Unfortunately, methods of this sort, while interesting in their own fashion, are inevitably hampered by the intervention of a noncyclic diradical pathway, which gives the same product as the forbidden Woodward–Hoffmann process.

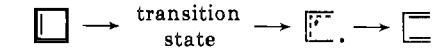
The Ring Opening of Simple Cyclobutenes. As we pointed out in the previous section, the isomerization of simple dienes suffers as a method for determining the energy advantage associated with the allowed cyclobutene ring opening because of the intervention of an interfering 1,2-diradical pathway. This problem can be solved in principle by beginning the sequence with the cyclobutene. For example, with *cis*-3,4-dimethylcyclobutene, one anticipates *cis,*-



trans-2,4-hexadiene by the allowed pathway.[13] Any *trans,trans*-2,4-hexadiene which appears (and which can be shown not to arise from trans impurity in the starting material or subsequent isomerization of the first formed cis,trans product) can be attributed to nonallowed reactions. Again this nonallowed pathway may be either a forbidden electrocyclic reaction or some new diradical pathway.

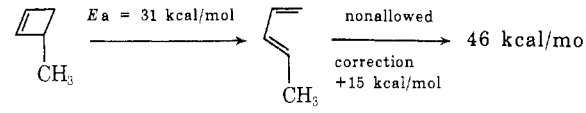
This most direct approach to the determination of the resonance stabilization of this electrocyclic reaction was carried out by a study of the pyrolysis of *cis*-3,4-dimethylcyclobutene.[7a] Vpc analysis of the ratio of *trans,trans*-2,4-hexadiene to the cis,trans isomer indicates a rate difference for formation of 6.1×10^{-5} at 280°, corresponding to $\Delta\Delta G^*$ of 10.7 kcal/mol. We note, however, that this allowed transition state is sterically destabilized relative to the nonallowed one, since the former requires moving a methyl "in," thus generating unfavorable nonbonded interactions, whereas the nonallowed path does not. It is difficult to evaluate completely this effect of moving a methyl group "in" as opposed to "out," but data of Frey and his coworkers suggest an added increment of 5–10 kcal/mol.[9,14] Thus the allowed transition state must experience electronic stabilization of at least 15 kcal/mol compared with the alternate pathway. If ΔS^* is greater for the nonallowed pathway, the estimate can only be corrected upward. The analysis can be refined by considering various models, such as a diradical, and correcting for substituent effects. Essentially identical conclusions are derived from these analyses.

Scheme I



The nature of the nonallowed transition state is a matter of some importance. While it is difficult, if not impossible, to ascertain experimentally whether the nonallowed reaction is diradical or a concerted forbidden reaction, it is possible to estimate the energy that a transition state leading to a diradical might be expected to have and to compare it with the observed energy. The diradical is taken to have no interaction between carbons 3 and 4 and carbons 2 and 3 (see Scheme I). This is precisely the procedure considered for a diene cis–trans isomerization. The energy of the diradical can be adequately estimated, as pointed out earlier, by subtracting one π bond from butadiene and adding the allyl resonance. Thus, we estimate the energy of the diradical at about 53 kcal/mol above butadiene or 41.5 kcal/mol above cyclobutene.[11a] Typically, small-ring diradicals require an apparent activation energy for closure, four-membered rings usually[5] in the neighborhood of 5 kcal/mol. Therefore, this transition state would probably have an energy of about 47 kcal/mol relative to cyclobutene, or again, about 15 kcal/mol above the activation energy of the allowed transition state.

A similar thermochemical approach for a different set of reactions leads to the same value for the energy of the nonallowed pathway.[15] The case of bicyclopentene is instructive. This compound is highly strained, but remarkably stable, presumably in part because the allowed opening of the cyclobutene would lead to the sterically inaccessible *cis,trans*-cyclopentadiene. The energy of a nonallowed pathway for this ring opening can be calculated by taking a cyclobutene model reaction which has no steric problems, 3-methylcyclobutene to 1,3-pentadiene, and adding on the energy increment for the nonallowed reaction. This estimate of 46 kcal/mol must be corrected for strain effects. This is done schematically in Figure 5 and yields an energy of 29 kcal/mol which may be compared to the known value of 27 kcal/mol. Other bicyclic compounds are also amenable to this type of treatment, thus giving added sup-



(13) R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 7557 (1969).

(14) (a) G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1546 (1966); (b) H. M. Frey, B. M. Pope, and R. F. Skinner, *ibid.*, **63**, 1166 (1967).

(15) (a) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968); (b) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

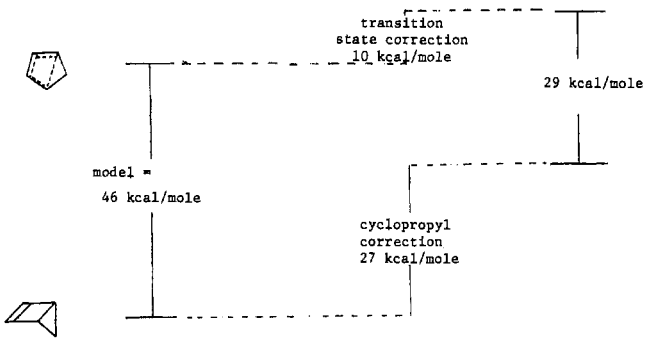


Figure 5. Thermochemical analysis of bicyclopentene ring opening.

port for the estimated value for the resonance energy associated with the allowed cyclobutene ring opening, 15–16 kcal/mol.

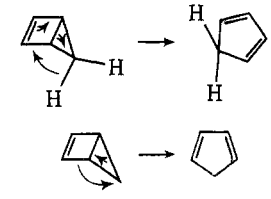
Finally, since a diradical or diradical-like pathway can be shown to be some 15 kcal/mol higher in energy than the allowed concerted pathway, we investigated the possibility of stabilizing the diradical by appropriate substitution, in an effort to make this path more competitive. To this end we synthesized the hitherto unknown *cis*-3,4-diphenylcyclobutene.[7b] Using the model in Scheme I for the diradical transition state one expects the energy of this pathway to be lowered by the benzyl resonance energy plus the difference between cinnamyl and allyl resonance energies. This would bring the energy of the stabilized diradical down to or below that of the transition state of the the allowed concerted path for the unsubstituted compound. Interestingly, we found the reaction of diphenylcyclobutene to be greater than 99% stereospecific, implying a predominantly concerted reaction. Obviously, the phenyl groups also significantly stabilize the concerted reaction. This is seen most dramatically in the acceleration of this reaction relative to model cases (E_a = 24.5 kcal/mol, diphenylcyclobutene; E_a = 33.0 kcal/mol, dimethylcyclobutene). Thus, we find that each phenyl group stabilizes the transition state electronically for the concerted reaction by about 5 kcal/mol.

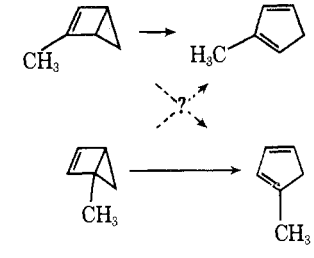
The origin of the stabilization by phenyl in a concerted reaction is of substantial interest. Perturbation theory suggests that substituent stabilization will be greatest in the least stable system, particularly if it is essentially diradical in character. Thus, we anticipated that the stabilizing effect of phenyl groups on the allowed transition state would probably not be as great as the effect on the nonallowed one. Nevertheless, the stabilization observed in the allowed cases, *ca.* 5 kcal/mol for each phenyl, is so large (almost half of the benzyl resonance energy) that it suggests that the interaction is an unusual one.

Examination of molecular models suggests that, during the course of the electrocyclic cyclobutene isomerization, appreciable electron density may occur in areas in which there is no bonding. That is, the "tails" of the hybrid orbitals at the termini of the π system do not overlap effectively with other orbitals in the cyclobutene–butadiene system. Thus, it might be expected that some electron density could be delocalized onto an appropriate substituent if the overlap and geometry were satisfactory.

Bicyclopentene → Cyclopentadiene: Is It Really Nonallowed? The first analysis of the energetics of the butadiene–cyclobutene surface was carried out using bicyclopentene as a model.[15] The preceding section, which outlines such a calculation, makes it clear that the energy required for ring opening of this strained bicyclic hydrocarbon is consistent with estimates of the energy required for the nonallowed Woodward–Hoffmann ring opening. The errors associated with thermochemical analyses are, however, frequently larger than 1 kcal/mol. An error of similar magnitude might also be reasonably associated with the experimental determination of this resonance energy using dimethylcyclobutene. It is well worth remembering that a substantial amount of chemistry can be hidden in a 1–2-kcal/mol energy range (1.4 kcal/mol translates into rate differences of 10 at room temperature). Previous experience indicates that a careful search for allowed pathways should be made before nonallowed hypotheses are accepted.

Just such a detailed search was begun in 1970 by Baldwin and coworkers, who recognized two possible allowed processes which might be involved. The first, involving hydrogen migration, was eliminated by deuterium labeling studies.[16] The second, a carbon rearrangement, finds support in recent work, however.[17] Methyl labels confirm the presence of a rearrangement process. At 30–50° in pentane solution ~10% of the rearranged product can be found starting with either isomer, with even more rearrangement found in the gas phase.[17b,c,18] This is consistent with a small amount of bond-switching rearrangement process. More recent work, however, indicates that a simpler postulate is likely. RRKM calculations by Flowers and Frey[19] indicate that the hot cyclopentadiene produced by ring opening of the highly strained bicyclopentene should rearrange rapidly by 1,5-hydrogen-shifting reactions to give the observed products. The cyclopentadiene, formed initially with ~60-kcal/mol excess energy, may not be completely deactivated thermally, even in solution, thus poten-





(16) J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Amer. Chem. Soc.*, **92**, 5249 (1970).

(17) (a) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970); (b) J. E. Baldwin and G. D. Andrews, *J. Amer. Chem. Soc.*, **94**, 1775 (1972); (c) G. D. Andrews, M. Davalt, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **95**, 5044 (1973); (d) See, however, S. McLean, D. M. Findlay and G. I. Dmitrienko, *J. Amer. Chem. Soc.*, **94**, 1380 (1972).

(18) J. I. Brauman, W. E. Farneth, and M. B. D'Amore, *J. Amer. Chem. Soc.*, **95**, 5043 (1973).

(19) M. C. Flowers and H. M. Frey, *J. Amer. Chem. Soc.*, **94**, 8636 (1972).

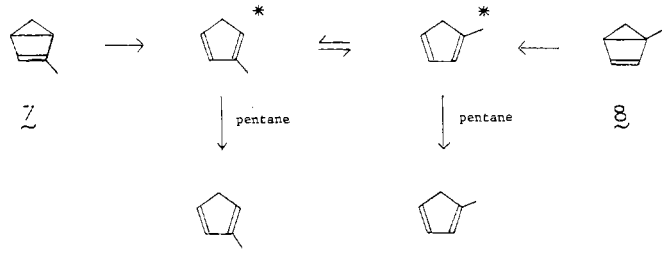


Figure 6. Chemical activation pathways in bicyclopentene pyrolysis.

Table I
Ratio of Rearranged to Unrearranged Methylcyclopentadiene at 50°

	Pressure, Torr, of pentane				
Reactant	<2	100	465	900	Solution
7	0.91	0.88	0.70	0.65	~0.1
8	0.85	0.76	0.54		~0.05

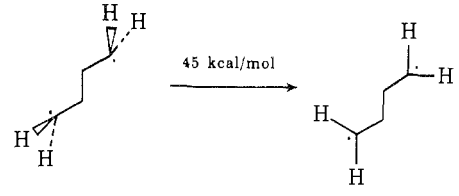
tially accounting for the observed rearrangement. Support for the contention that chemical activation processes are important in this rearrangement is derived from a study of the pressure dependence of the gas-phase pyrolysis.[18] As is evident from reference to Figure 6 and Table I, as the pentane pressure is increased, smaller ratios of rearranged to unrearranged isomers are found. Thus, in this case, a nonallowed pathway appears to be the major course of the ring-opening reaction. Again, it remains unclear, and is perhaps impossible to determine in this system, whether a diradical or a concerted, forbidden pathway is responsible for the nonallowed component. While it may be possible to distinguish these possibilities theoretically, no experimental basis for determining this difference is obvious to us in this system.

Quantum Calculations of the Cyclobutene–Butadiene Surface. In recent years, new generation molecular orbital and valence bond procedures have been applied to a variety of problems of interest to the organic chemist. The electrocyclic transformations discussed in this review involve both small-ring chemistry and an apparent concerted process, thus combining two areas frequently explored by computational procedures. Several groups have performed such calculations on the cyclobutene–butadiene system.[20]

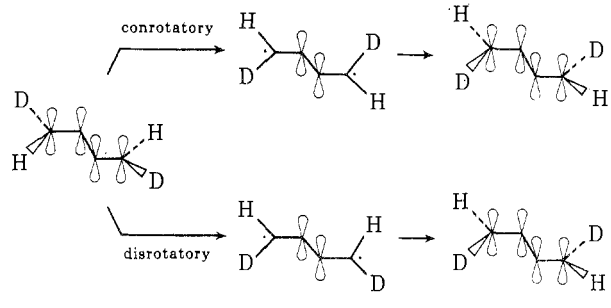
All such calculations performed to date seem to possess a common feature. Extensive stretching of the carbon–carbon single bond is apparently required to precede rotation of the methylene group in a conrotatory manner. Several workers have noted this effect with stretching to as far as 2.3 Å required before twisting can be initiated. Buenker and coworkers[20c] have noted that part of this effect can be alleviated by allowing substantial ring torsion during the opening process.

That nonplanar conformations reduce this effect encourages us to postulate through-bond coupling of the type noted by Hoffmann as responsible for this trend. We have previously noted in connection with other systems that such through-bond coupling appears to be badly overestimated by the CNDO procedure, an effect possibly common to many procedures.

As an example, the barrier to terminal bond rotation in the 1,4 diradical is calculated to be extraordinarily high.[21] Since no one seriously believes that the barrier is as high as the 45 kcal/mol calculated, and at least some experimental evidence exists to the contrary, a serious flaw in the method would appear to be revealed by these calculations.



An even more dramatic example of the importance of through-bond effects as determined by calculation was found in the following manner. As a matter of curiosity the double isomerization in *s-trans*-butadiene was examined by the CNDO method. Here both conrotatory and disrotatory modes may be envisioned. Because of the peculiar combination of loss of π energy and gain of through-bond coupling, these two paths are not energetically equivalent in reaching the common midpoint. The conrotatory path was favored by as much as 60 kcal/mol at one point (72°) on the twisting surface.[22] This interesting prediction has not been tested experimentally, but again it seems unlikely that such a large effect would be confirmed, even though the qualitative trend may be sound.



We conclude with a word of caution based on our experience with the two systems above. Any conformation which allows through-bond coupling may well overemphasize that effect using a molecular orbital method. This overemphasis may be the responsible factor in the requirement for extensive stretching of the cyclobutene before rotation of methylenes (and loss of through-bond coupling) can occur. Substantial added work on these methods may be required before such calculations become quantitatively reliable in predicting the shape of reaction potential surfaces.

Summary. The ring–chain tautomerism between cyclobutene and butadiene is perhaps the most familiar example of an allowed Woodward–Hoffmann process. This transformation invariably is discussed in every attempt to rationalize or teach the Woodward–Hoffmann orbital symmetry concepts. This

(20) (a) J. W. McIver, Jr., and A. Komornicki, *J. Amer. Chem. Soc.*, **94**, 2625 (1972); (b) G. Feler, *Theor. Chim. Acta*, **12**, 412 (1968); (c) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **93**, 2117 (1971); (d) M. J. S. Dewar and S. Kirscher, *J. Amer. Chem. Soc.*, **93**, 4290, 4291, 4992 (1971).

(21) L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

(22) L. M. Stephenson and R. V. Gemmer, unpublishable results.

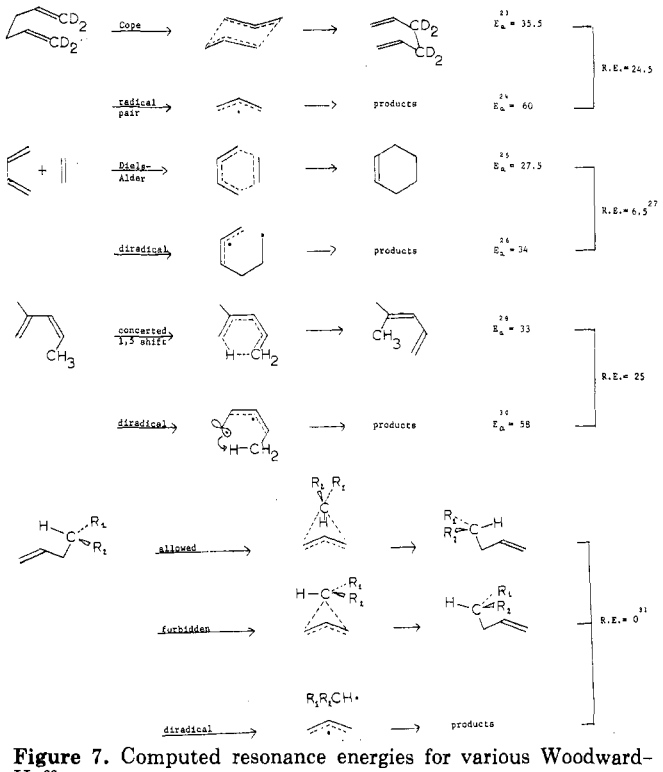


Figure 7. Computed resonance energies for various Woodward-Hoffmann processes.

popularity is due in large part to the existence of a geometrically well defined (and easily visualized) alternate, forbidden, electrocyclic pathway. Thus it is exceedingly simple to set up a nonallowed strawman, the disrotatory ring opening, and show that the allowed, conrotatory path is to be preferred.[3a,b]

This easily *visualized* nonallowed pathway is not easily *evaluated* from an energy standpoint. In many other apparent orbital-symmetry-controlled processes such an evaluation is simple since the most logical alternative involves fully bond-broken species, diradicals or radical pairs (Figure 7). It can be seen that resonance energies evaluated for a few typical processes vary from 0 to 25 kcal/mol depending in some cases on which diradical or bond-broken model is chosen to represent the alternate transition state.

In the present case it has been possible to evaluate an energy difference of ~15 kcal/mol between an allowed conrotatory process and *some* nonallowed pathway. In contrast to the cases noted briefly above, it is not possible to say with any degree of certainty whether the nonallowed path is diradical-like or a forbidden, concerted transformation (if indeed such a distinction can be made). As we have pointed out, the energy requirement of the nonallowed reaction corresponds closely to that which one would associate with a pathway leading to a structure containing an allylic and a noninteracting radical center, but such a coincidence is not strong evidence for the existence of any species. This latter distinction is beyond the scope of most experiments which have been designed to probe the energetics of Woodward-Hoffmann systems, and only systems as complex as those studed by Berson[31] appear to be capable of dealing with this problem in principle.

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(23) W. von E. Doering and V. Toscano, unpublished work, quoted in ref 11b.

(24) Calculated by assuming $DH°$ = 82 kcal/mol − 2 allylic resonance energies (2 × 11 kcal/mol) = 60.

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

(26) The ΔH^* for the diradical reaction is most conveniently calculated for the reverse reaction. Thus the heat of formation for the diradical is $\Delta H_f°$(cyclohexene) + $DH°$(C-C bond) − methylallyl resonance energy; −1.7 kcal/mol + 82 kcal/mol − 13 kcal/mol 67 kcal/mol. An additional $DH°$ may be required to break the second bond and reach the transition state for the forward (association) reaction. The cleavage reaction of the 1,4-diradical to two ethylenes is the closest analogy with an apparent $DH°$ of 6 kcal/mol. We assume this value is applicable here. This gives ΔH^* for the reverse reaction of 73 kcal/mol. Subtracting $\Delta H_f°$ of 26.3 kcal/mol (butadiene) and 12.5 kcal/mol (ethylene) gives ΔH^* for the forward reaction of 34 kcal/mol.

(27) The data of Bartlett and Schueller[28] are interesting in this regard. These workers find 0.02% vinylcyclobutane in the product from this reaction along with 99.98% cyclohexene. If *all* the vinylcyclobutane is derived from the diradical species, and all the cyclohexene comes from a concerted reaction, then the Diels-Alder transition state RE ≃ 7 kcal/mol. It is probably more reasonable to view this number as an upper limit.

(28) P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6071 (1968).

(29) H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 4770 (1965).

(30) This model is calculated in two steps. Step 1, the formation of the diradical, should require slightly less energy than that discussed earlier for 1,2-diradical isomerization in butadiene. We estimate 50 kcal/mol. The H-atom transfer step is presumed to be strain free and to require the 8 ± 2 kcal/mol known for many exothermic hydrogen transfers of this sort (see ref 5, p 101).

(31) For a complete discussion of such a reaction see J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).