

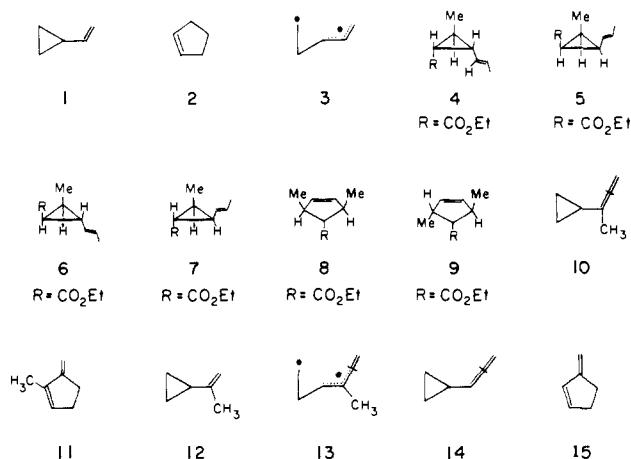
# Mechanism of the Vinylcyclopropane Rearrangement. The Rearrangement of Cyclopropylallene and MINDO/3 Calculations<sup>1</sup>

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**Abstract:** The rate of rearrangement of 3-cyclopropyl-1,2-butadiene to 2-methyl-3-methylenecyclopentene has been measured over a range of temperature,  $k = 10^{12.8} \exp(-41,500/RT)$ . The reaction is much faster than the rearrangement of vinylcyclopropane to cyclopentene. MINDO/3 calculations for the latter, and for the rearrangement of cyclopropylallene to 3-methylenecyclopentene, are reported. The reactions are "forbidden" biradicaloid processes. The difference in rate between them is shown to be due to a corresponding difference in heat of reaction.

The thermal rearrangement of vinylcyclopropanes to cyclopentenones (e.g., **1**  $\rightarrow$  **2**) is a well-known reaction which has been extensively studied.<sup>2-9</sup> It appears to be a unimolecular process with an activation energy of 49.7 kcal/mol. According to conventional ideas concerning the thermochemistry of biradicals,<sup>10</sup> this amount of energy should be sufficient to cleave one of the bonds in the cyclopropane ring of **1** to form the biradical **3**,<sup>11</sup> and the intermediacy of **3** has also been supported by studies of the degenerate rearrangement of **1**.<sup>12</sup> A concerted mechanism would moreover be expected<sup>13</sup> to involve inversion of the migrating methylene group, a type of process normally observed only in rather constrained systems.



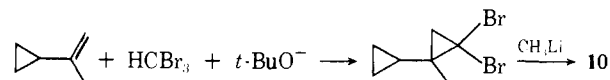
Mazzocchi and Tamburin<sup>14</sup> have studied the rearrangements of the four stereoisomeric 2-methyl-3-propenylcyclopropanecarboxylic esters **4-7** to the 3,5-dimethylcyclopentenecarboxylic esters **8** and **9** (the all-cis isomer was not formed in detectable amount due, no doubt, to steric hindrance). If the reactions were concerted and took place with inversion at the migrating  $\text{CHCOOEt}$  center, **4** and **6** should have given exclusively **8**, while **5** and **7** should have given exclusively **9**. In fact comparable amounts of **8** and **9** were formed in all cases. Moreover the main products of the reaction were open-chain hexadiene derivatives that could very well have arisen by hydrogen migration in biradical intermediates. These results were therefore held to support the biradical mechanism.

Since the carbethoxy group is a good radical stabilizer, it is quite possible that the reactions of **4-7** might be untypical, a biradical mechanism being favored by stabilization of the biradical intermediate.<sup>15</sup> It is also rather difficult to see

why the reaction should be even stereoselective if it involves genuine biradical intermediates.

We became interested in this problem through a study of the rearrangement of 3-cyclopropyl-1,2-butadiene (**10**) to 2-methyl-3-methylenecyclopentene (**11**). Certain unexpected features of the reaction led us to study it and the related rearrangement of **1** to **2**, using the MINDO/3<sup>16</sup> semiempirical SCF-MO method. Since the two investigations were thus closely related, we are publishing them together.

**The Rearrangement of 3-Cyclopropyl-1,2-butadiene (10).** While the rearrangement of vinylcyclopropanes is a well-known reaction, no one as yet seems to have examined the possibility of an analogous rearrangement in the case of a cyclopropylallene. Since we were also interested in compounds of this type in another connection, we prepared 3-cyclopropyl-1,2-butadiene (**10**) by the following route:



Preliminary studies showed not only that **10** rearranged to the expected 2-methyl-3-methylenecyclopentene (**11**) but also that the reaction took place much more easily than the corresponding rearrangement of **1** to **2**. This difference could not be attributed to the methyl substituent in **10** because it is known that 2-cyclopropylpropene (**12**) rearranges almost at the same rate as **1**, the activation energy for rearrangement of **12** being less than that for **1** by only 0.3 kcal/mol.<sup>9</sup>

This result seemed inconsistent with the biradical mechanism because it is difficult to see any reason why the strength of a bond in the three-membered ring of a cyclopropylallene should be any less than that in an analogous vinylcyclopropane. Thus the biradical **13** that would be formed from **10** should not be resonance stabilized to any greater extent than **3**, and its formation should be hindered by the fact that the breaking bond in **10** of  $\text{sp}^2\text{-sp}^3$  type and so stronger than the corresponding  $\text{sp}^3\text{-sp}^3$  bond in **1**.<sup>17</sup> Nor can the difference be attributed to hyperconjugation; for in each case (i.e., **1**  $\rightarrow$  **3** and **10**  $\rightarrow$  **13**), formation of the biradical leads to just one additional hyperconjugative ( $\text{sp}^2\text{-sp}^3$ ) interaction.

In view of the apparent interest of this novel rearrangement, we measured its rate in the gas phase over a range of temperatures and so determined the corresponding Arrhenius parameters. These, and the individual rate constants, are shown in Table I. It will be seen that the preexponential factor is close to that reported for the rearrangement of **1** ( $\log A$  is 13.5), the greater rate being due to a large decrease (8.2 kcal/mol) in the activation energy.

These results seemed to throw considerable doubt on the suggested biradical mechanism for such rearrangements. Apart from the arguments given above, it would be difficult to explain, on this basis, the apparently "normal" value of the preexponential factor; for conversion of **2** to **3** should lead to a large increase in flexibility, due to an additional internal rotation and a reduced torsional vibration frequency.

**MINDO/3 Calculations.** In view of these difficulties, we decided to study the conversion of **1** → **2** and of **10** to **11** using MINDO/3.<sup>16</sup> MINDO/3 is now a well-established procedure for the study of reaction mechanisms, having given very satisfactory results in a large number of cases.<sup>18</sup> While these had included both "allowed" and "forbidden" reactions of supposedly pericyclic types, none had involved a sigmatropic process; this of course provided us with a further incentive.

We decided to study the conversion of cyclopropylallene (**14**) to 3-methylenecyclopentene (**15**), rather than that of **10** to **11**, since it seemed clear that the methyl substituent could not affect the rate to any great extent and since its inclusion would have considerably increased the cost of the calculations. We therefore first studied the conversions of **1** to **2**, and of **14** to **15**, taking the length ( $r$ ) of the breaking bond as our reaction coordinate. For each value of  $r$ , the energy was minimized with respect to all other coordinates using our standard procedure.<sup>16,35</sup>

As we have frequently observed<sup>36</sup> in the past for "forbidden" reactions, these processes showed "chemical hysteresis",<sup>36</sup> the forward and backward paths differing. The reaction was clearly trying to follow a "forbidden" path with retention of configuration at the migrating methylene. Since such a reaction involves the interconversion of lumomers,<sup>37</sup> with a concomitant HOMO/LUMO crossing, the potential surface contains two valleys.<sup>36</sup> One corresponding to homomers<sup>37</sup> of the reactant and the other to homomers of the product. The valleys are separated by a ridge corresponding to the biradical structures that mark the HOMO/LUMO crossing. In this case, the geometrical constraints are such as to make the transition state a point on the biradical ridge. Since the relevant part of the potential surface was therefore evidently biradical like, we included configuration interaction (CI) with the lowest doubly excited configuration.<sup>38</sup> As previously, inclusion of CI lowered the potential surface in the vicinity of the biradical ridge but did not alter its two-valley structure.

A plot of the calculated energy (with inclusion of CI) vs.  $r$  for the forward and backward reactions (Figure 1) consisted of two intersecting lines. Since these continued to high energies on either side of their intersection, it was evident that the lowest point in the intervening ridge must lie between the structures corresponding to the point where the lines in Figure 1 cross.<sup>39</sup> We used to locate such transition states by tedious grid searches,<sup>35</sup> using two or more different reaction coordinates. Now, however, they can be located directly by minimizing the scalar gradient.<sup>40</sup> To do this, one has to have an initial approximation to the structure of the transition state; we used as our initial structure an average of the two corresponding to the crossing point of the lines in Figure 1. Rapid convergence was obtained in both cases; the calculated structures of the two transition states are shown in Figure 2.

The calculated activation energies agreed quite well with experiment; i.e.:

$$\mathbf{1} \rightarrow \mathbf{2}; \Delta E^\ddagger (\text{calcd}, 48.4) = 49.7 \text{ kcal/mol} \quad (1)$$

$$\mathbf{14} \rightarrow \mathbf{15}; \Delta E^\ddagger (\text{calcd}, 44.6) \text{ (for } \mathbf{10} \rightarrow \mathbf{11}) = 41.5 \text{ kcal/mol} \quad (2)$$

Table I. Rearrangement of 3-Cyclopropyl-1,2-butadiene

$T, ^\circ\text{C}$	$10^4 K, \text{sec}^{-1}$	Arrhenius parameters	
		$E, \text{kcal/mol}$	$\text{Log } A$
280.0	2.51	41.5	12.8
290.0	4.90		
300.0	9.31		

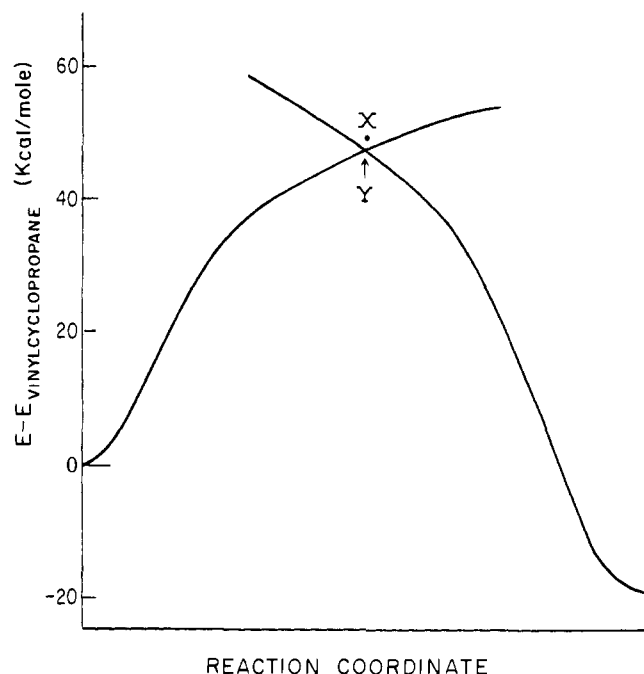


Figure 1. Section of the potential surface for the "forbidden" conversion of **1** to **2**. Each line represents the bottom of a valley corresponding to reactant or product. X marks the position of the true transition state on the intervening ridge.

The agreement may indeed be better than it seems; for the methyl substituent in **10** certainly cannot increase  $\Delta E^\ddagger$  and may well reduce it more than does the methyl group in **12**. Our calculations therefore predict both reactions to be "forbidden" processes in which the biradical intermediate is the transition state. As an additional check, we examined the "allowed" conversion of **1** → **2** in which inversion occurs at the migrating methylene; while we did not locate the transition state at all exactly, we established that it must be of very high energy. Here the "allowed" process should be truly forbidden.<sup>43</sup>

The favored path for the reactions should therefore involve retention of configuration of the migrating group. However, the calculated structures of the transition states (Figure 1) show that the interactions between the two radical centers must be very weak. Very little extra energy will be required to pull them apart enough for rotation to occur, particularly if a radical-stabilizing substituent is introduced into the migrating methylene. Our calculations therefore account very nicely for the rearrangements of **4**–**7** which we referred to earlier.<sup>14</sup>

While our calculations reproduce the experimental results in a satisfactory manner, in particular the fact that **10** rearranges so much faster than **1**, we still have to explain why this is the case. Let us then consider in more detail the features of the two potential surfaces revealed by our calculations.<sup>44</sup>

Consider Figure 1. As we have remarked, the two lines represent sections of the potential surface along the bottoms of the reactant-like and product-like valleys. The minimum

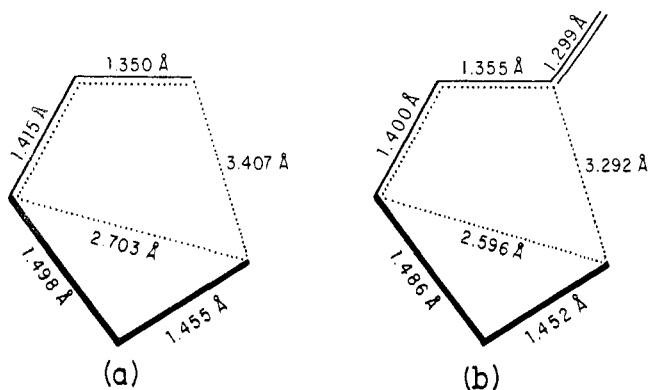


Figure 2. Calculated transition state geometries for: (1)  $1 \rightarrow 2$ ; (b)  $14 \rightarrow 15$ .

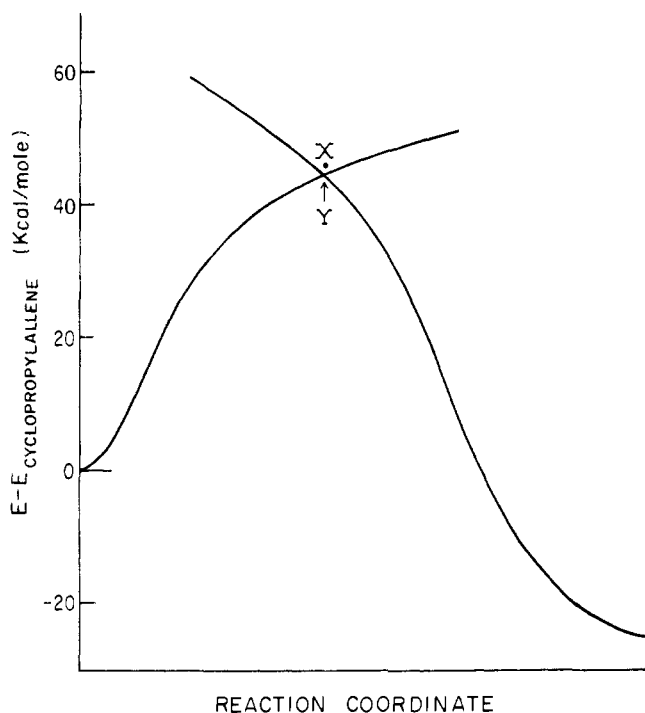


Figure 3. Section of the potential surface for the forbidden conversion of  $14$  to  $15$ . Each line represents the bottom of a valley corresponding to reactant or product. X marks the position of the true transition state on the intervening ridge.

energy reaction path has to cross from one to the other over the intervening biradical ridge. Since the apparent crossing point of the lines (Y in Figure 1) corresponds to structures which are very similar, we would expect the ridge at this point to be very low; in fact, the transition state (X in Figure 1) lies very little above Y in energy (1.6 kcal/mol). The corresponding plot for  $14 \rightarrow 15$  (Figure 3) is precisely analogous; in this case, the transition state (X) lies 1.8 kcal/mol above the crossing point Y.

Now these plots are very reminiscent of the Evans-Polanyi approach to reactivity.<sup>45</sup> There one plots a "bond-breaking" curve representing the change in energy of the reactant as bonds broken during the reaction progressively weaken, and a "bond-forming" curve representing the change in energy of the system, in which all breaking bonds have broken, as the new bonds form. Both curves are plotted against a common reaction coordinate; the crossing point is taken as an approximation to the transition state.

Now the "bond-forming" curve can equally be regarded as a "bond-breaking" curve for the reverse reaction. The

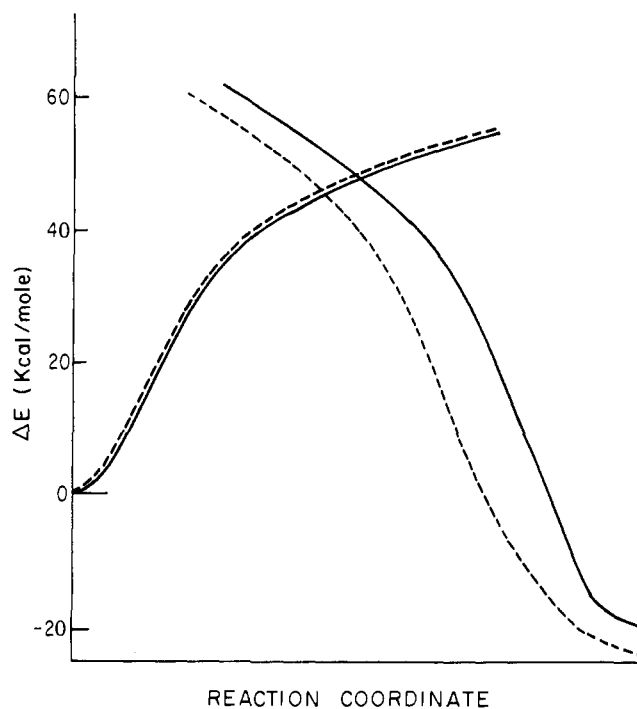


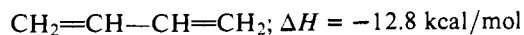
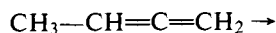
Figure 4. Superposition of the reaction coordinate plots for  $1 \rightarrow 2$  and  $14 \rightarrow 15$  displaced to show energies relative to the reactant ( $1$  or  $14$ ).

two "bond-breaking" curves therefore represent the change in energy of the reactants, or of the products, that would take place with successive changes in the reaction coordinate, if no reaction occurred. Thus the forward "bond-breaking" curve corresponds precisely to the "reactant-type" curves in Figures 1 and 3 and the reverse "bond-breaking" curve to the corresponding "product-type" curves.

In a normal "allowed" reaction, a single valley leads from reactant to product; the "reactant-like" and "product-like" valleys meet. In resonance terminology, the transition state is then a hybrid of reactant-like and product-like structures; it is correspondingly resonance stabilized<sup>45,46</sup> and its energy is correspondingly lower than the intersection of the reactant-like and product-like plots. In the case of a "forbidden" reaction, however, the "reactant-like" and "product-like" plots correspond to sections of the potential surface along two different valleys. If the constraints are such that the transition state corresponds to a point on the "biradical" ridge separating them, this should lie only a little above the apparent intersection of the two plots (cf. points X and Y in Figures 1 and 3). The intersection point (Y) will now lie *below* the true transition state (X) but only a little below; reactions of this type should therefore follow the BEP (Bell-Evans-Polanyi)<sup>47</sup> relation accurately, the variations in the activation energies of different reactants of a common type being proportional to the corresponding heats of reaction.

If we plot the curves of Figure 1 and Figure 3 together, taking the energy of the reactant as the energy zero, we find (Figure 4) that the reactant-type curves are almost identical, and that the product-type curves are almost parallel, as the BEP principle requires. We can now see why  $(10 \rightarrow 11)$  is much faster than  $(1 \rightarrow 2)$ . It is faster because it is more exothermic. The greater exothermicity in turn is due to simple conjugation effects. In  $(1 \rightarrow 2)$ , the only conjugative change is of a single  $sp^3$ - $sp^3$  CC bond to  $sp^3$ - $sp^2$  type. In  $(10 \rightarrow 11)$ , or  $(14 \rightarrow 15)$ , we also convert a  $sp^3$ - $sp^3$  CC bond to  $sp^2$ - $sp^2$  type, but we in addition convert a cumulated (1,2) diene into a conjugated one. The corresponding de-

crease in  $\Delta H$  can be estimated from thermochemical data for the butadienes.<sup>48</sup>



The difference between the observed activation energies for (1  $\rightarrow$  2) and (10  $\rightarrow$  11) is 8.2 kcal/mol. The ratio of this to the estimated difference in heat of reaction ( $-12.8$  kcal/mol) is 0.64, a reasonable value for a BEP factor.<sup>49</sup>

So far we have considered only rearrangement of 1 in which the migrating methylene group retains its geometry. Here the HOMO/LUMO crossing involves an inversion of relative phase of the AOs of the nascent CC bond. Alternatively, the necessary phase inversion can take place by rotation of the methylene group. We have also studied the latter process and find that the corresponding activation energy is virtually identical with that for the former. This explains why rearrangements of vinylcyclopropanes take place with almost complete loss of configuration.

## Experimental Section

**1-Methyl-1-cyclopropyl-2,2-dibromocyclopropane.** Bromoform (227.7 g, 0.90 mol) was added dropwise to a stirred slurry of potassium *tert*-butoxide (112.1 g, 1.00 mol), 2-cyclopropylpropene (58.5 g, 0.71 mol), and dry pentane (0.5 l.) below 0° and the mixture stirred for 6 hr. Water (400 ml) was then added and the organic layer separated, washed with water (3  $\times$  100 ml), dried (MgSO<sub>4</sub>), and distilled, giving the *dibromide* (106.1 g, 57%): bp 52.0–53.0° (0.2 mm);  $n_D^{20}$  1.5349; mass spectrum ( $m/e$ ) 252, 254, 256; ir (neat liquid), 690, 830, 864, 978, 1017, 1044, 1058, 1080 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  1.35 (s, 3 H), 1.23 (d, 2 H), 0.8–0.1 (m, 4 H). Anal. Calcd for C<sub>7</sub>H<sub>10</sub>Br<sub>2</sub>: C, 33.08; H, 3.97. Found: C, 32.92; H, 3.98.

**3-Cyclopropyl-1,2-butadiene (10).** A solution of methylolithium (4.4 g, 0.2 mol) in dry ether (125 ml) was added dropwise to one of 1-methyl-1-cyclopropyl-2,2-dibromocyclopropane (44.5 g, 0.169 mol) in dry ether (200 ml) with cooling (ice bath). After 30 min, water (50 ml) was added and the organic layer washed with water (3  $\times$  100 ml), dried (MgSO<sub>4</sub>), and distilled. The *allene* (9.0 g, 62.9%) was collected at 39.0–40.0° (67 mm);  $n_D^{20}$  1.4652; mass spectrum ( $m/e$ ) 94; ir (neat liquid), 821, 861, 1021, 1965 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  4.60 (m, 2 H), 1.67 (t, 3 H), 1.30–0.82 (m, 1 H), 0.80–0.15 (m, 4 H). Anal. Calcd for C<sub>7</sub>H<sub>10</sub>: C, 89.29; H, 10.71. Found: C, 89.17; H, 10.61.

**Kinetic Measurements.** The rearrangement of 10 was carried out in hexane solution (1.07  $\times$  10<sup>-5</sup> M) containing cyclooctane (6.5  $\times$  10<sup>-6</sup> M) as internal standard for GLC analysis. Degassed samples (0.1 ml) were sealed in evacuated Pyrex tubes (9 cm  $\times$  6 mm i.d.) and heated in a thermostated silicon bath ( $\pm 1^\circ$ ). Analyses were carried out by GLC on a 100-ft MBMA capillary column using a flame ionization detector. The chromatograph was calibrated using authentic samples of 10 and 11. The reactions followed first-order kinetics. The rate constants were calculated by standard procedures, using a computer program written by Dr. M. Short.

## References and Notes

- This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.
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- The lines represent cross-sections of the potential surface along the bottoms of two different valleys. Their intersection corresponds to the most stable reactant-like and product-like structures having the corresponding common value of  $r$ .
- This procedure was first introduced by McIver and Komornicki.<sup>41</sup> We used a versatile program developed here.<sup>42</sup>
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- This is also the case<sup>34</sup> in the  $\pi$ -cycloolimerization of ethylene to cyclobutane where the "allowed" [<sub>2s</sub> + <sub>2a</sub>] mechanism has a very much higher activation energy than the "forbidden" one.
- A common criticism of such arguments is that, since potential surfaces are in general inaccessible to experiment, one has no way of telling how valid our calculated ones are. This criticism applies of course to all current theoretical procedures. MINDO/3 has at least been shown to give satisfactory estimates of the energies and geometries of a very wide range of molecules including "nonclassical" structures, radicals, and triplet states. Since it has also given good estimates of activation energies for a large number of varied reactions, there seems more justification for accepting the corresponding estimates of the geometries of potential surfaces than there would be in similar calculations by other available procedures.
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- Our discussion in this paper has been based on the assumption that the rearrangements of 1 and 14 are both suprafacial. It seems now to be generally accepted that antarafacial allylic rearrangements are not feasible in systems of this kind. We have in fact studied this process in related systems where it should be more favorable than here and found it to have a very high activation energy. This, like the cycloolimerization of ethylene,<sup>34</sup> is another case where an "allowed" reaction is less favorable than a corresponding "forbidden" one, for geometrical reasons. In view of these considerations, and in view of the good agreement between our calculated activation energies for rearrangement of 1 and 14 and those observed, it seemed a pointless waste of computing time to examine the corresponding antarafacial reactions.