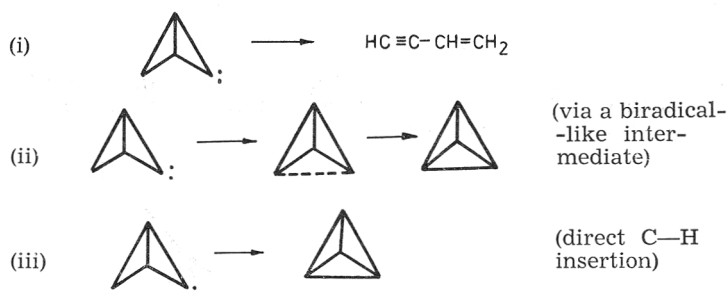# MINDO/3 Study of the Thermal Rearrangements of Bicyclobutanylidene

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The following three rearrangements of bicyclobutanylidene have been studied using the MINDO/3 method:

It is found that path (i), which is concerted and stereospecific, is favored both thermodynamically and kinetically, in agreement with experimental results. In addition, paths (ii) and (iii) are found to be competitive with each other and both are highly energetic due to steric effects, with activation energy being about 50 kcal/mol.

INTRODUCTION

Recently, there has been considerable interest in carbene rearrangements as routes to high-energy species.[1] The work presented here consists of theoretical investigations on some of the possible rearrangements of the bicyclic carbene, bicyclobutanylidene, **1**, which has been generated by addition of atomic carbon[2]
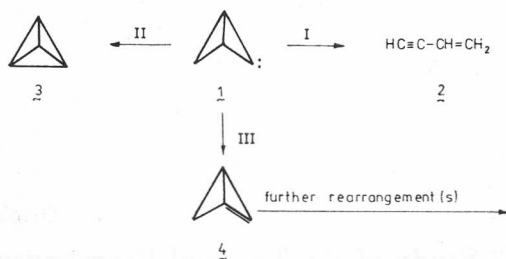

1

or carbon suboxide[3,4], $O=C=C:$, to cyclopropenes.

There appear to be three possible rearrangement paths for **1**:

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Bond breaking with electron rearrangement (path I) gives vinylacetylene (2), which has been observed as the major product by Shevlin and Wolf[4]. Path II leads, via a C—H insertion, to tetrahedrane, 3, which has been postulated as an intermediate in the gas phase photolysis of carbon suboxide in the presence of cyclopropene[4]. Finally, path III leads to bicyclo[1.1.0]butene, 4, via a 1,2-hydrogen migration. Species 4 has not been investigated theoretically, but it may be as energetic as bicyclo[1.1.0]but-1,3-ene, which has been studied by Hehre and Pople[5] using ab initio MO methods, and will probably rearrange further under the condition of its formation. In this work, only paths I and II have been studied.

<div align="center">METHOD OF CALCULATION</div>

The semi-empirical molecular orbital model used in this study is the well-tested MINDO/3 method[6]. The calculations were performed on the IBM 3031 computing system at the Chinese University of Hong Kong.
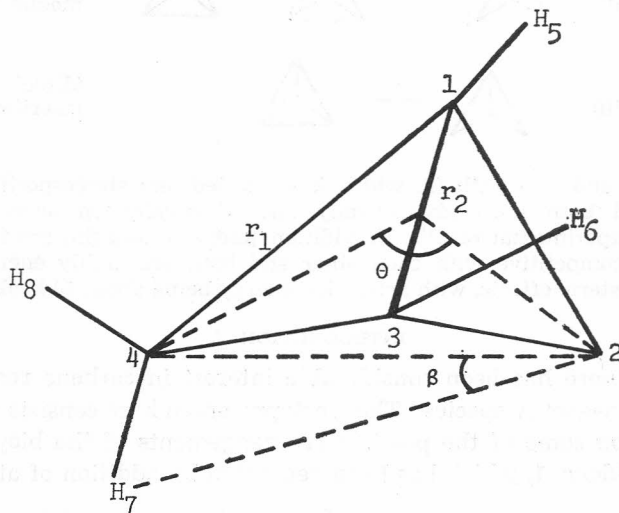

Figure 1. Structural parameters for the rearrangements of bicyclobutanylidene.

The structural parameters for the rearrangement paths I and II are defined in Figure 1. For the rearrangement $1 \rightarrow 2$, i. e., path I, r_1 (1.4 Å—3.0 Å) and r_2 (1.5 Å——3.0 Å) were chosen as reaction coordinates for the potential energy surface. All other geometrical parameters were optimized. The potential energy surface of $1 \rightarrow 3$, i. e., path II, was obtained from the energy curves $E(\beta)$ for each given value of Θ, ranging from 60° to 180°, with C_s symmetry assumed throughout and a minimum 2×2 configuration interaction treatment included.

RESULTS AND DISCUSSION

Calculated structural parameters of **1** are shown in Figure 2; the MINDO/3 results of bicyclobutane[7] are also presented for comparison. In addition, the MINDO/3 charges on C_1 to C_4 are 0.103, —0.179, 0.103, and 0.046, respectively. Judging from the optimized geometry and the charge distribution, the electronic
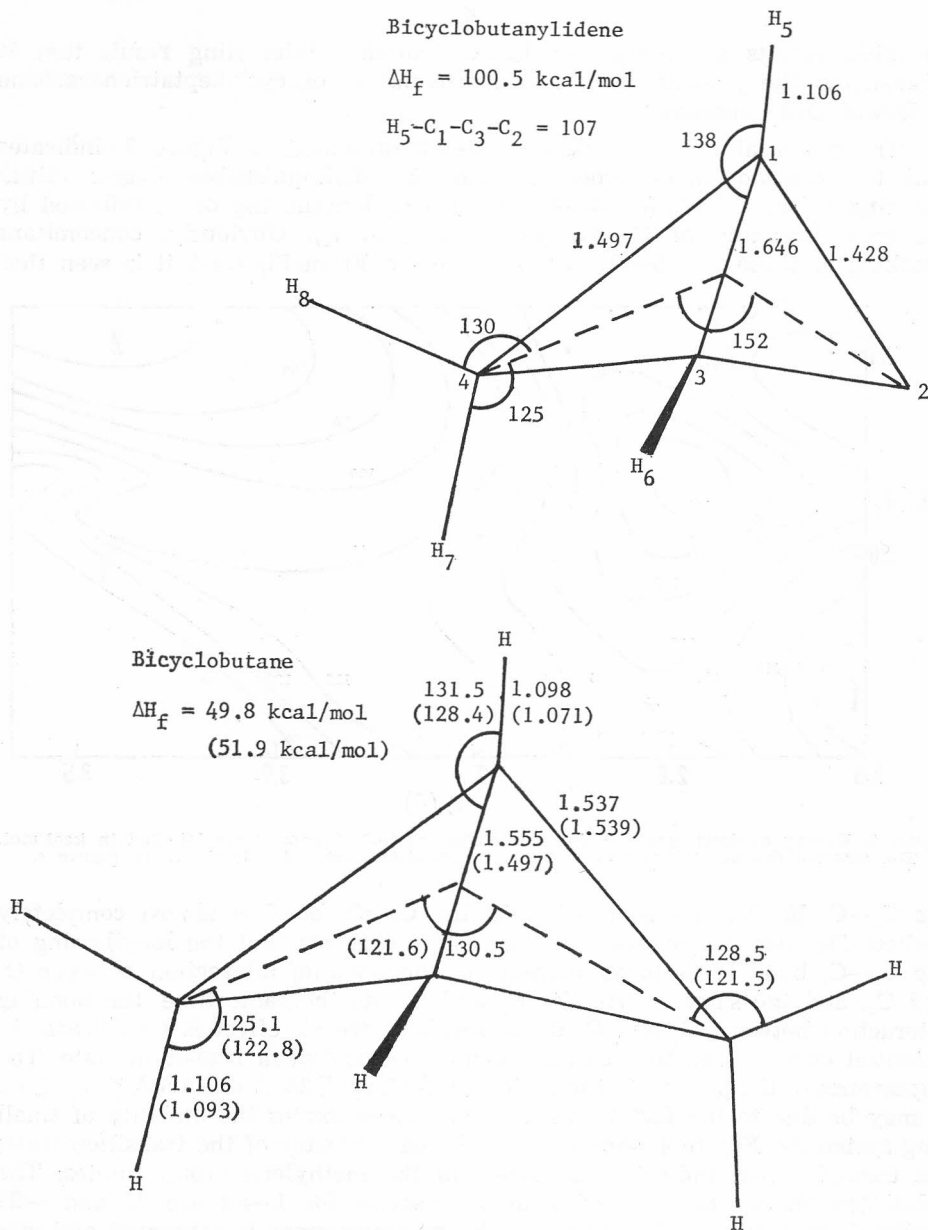

Figure 2. Calculated geometries of **1** and bicyclobutane (observed values[7] for the latter are given in brackets). Bond lengths are in Å and angles in degrees.

structure of **1** may be more properly described as **5**, in agreement with the

5

ab initio results of Hehre and Pople[5]. Another interesting result that is relevant to the present work is the calculation of cycloheptatrienacarbene of Dewar and Landman.[8].

The potential energy surface of **1 → 2** presented in Figure 3 indicates that the rearrangement proceeds with two distinguishable stages: initial breaking of the C_1—C_4 (or C_3—C_4) bond, i. e., lengthening of r_1, followed by the bond breaking of C_1—C_3 (lengthening of r_2). Obviously, concomitant breaking of these two bonds is very unlikely. From Figure 3 it is seen that
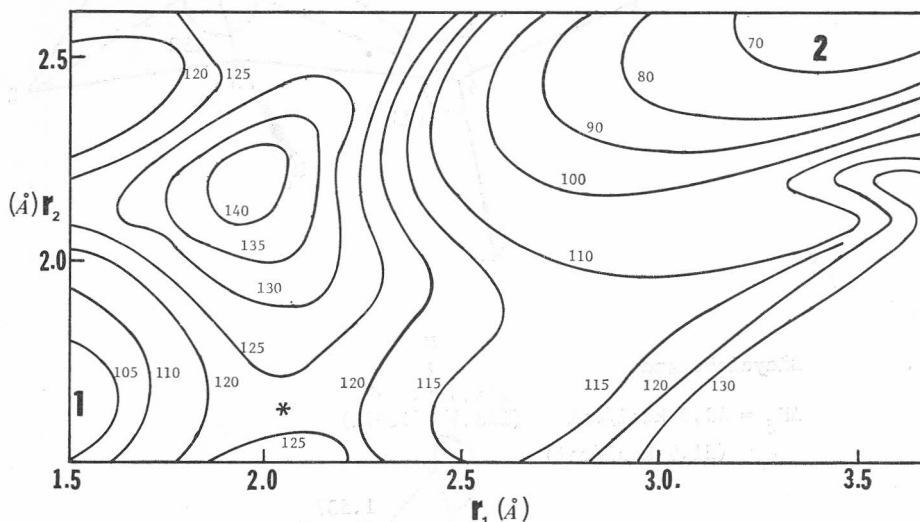

Figure 3. Energy contour map for the rearrangement 1→2. Contours are labelled in kcal/mol. The asterisk denotes the transition state, the geometry of which is shown in Figure 4.

the C_1—C_3 bond remains intact until the C_1—C_4 bond is almost completely broken. Detailed examination of the results suggests that the lengthening of the C_1—C_4 bond leads to an increase in the bonding interaction between C_1 and C_2, and the same is true for C_3 and C_4. At the same time, the bonding interaction between C_2 and C_3 decreases. The overall effect is an increase in potential energy, i. e., the rearrangement proceeds via a transition state. The appearance of the plateau in the region 2.5 Å $< r_1 <$ 2.9 Å and 1.5 Å $< r_2 <$ 1.8 Å may be due to the fact that MINDO/3 overestimates the stability of small ring systems[7,9]. Figure 4 shows the predicted geometry of the transition state; the curved arrow indicates the direction the methylene group rotates. The calculated energy barrier and heat of reaction for **1 → 2** are 22 and —39 kcal/mol, respectively. In summary, the rearrangement is concerted and stereospecific as depicted in Figure 5.
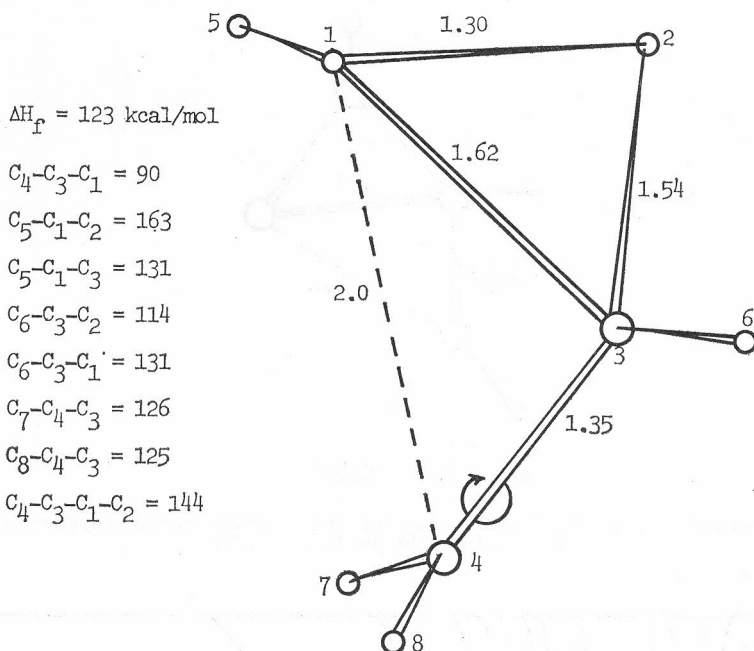
$\Delta H_f = 123$ kcal/mol

$C_4-C_3-C_1 = 90$

$C_5-C_1-C_2 = 163$

$C_5-C_1-C_3 = 131$

$C_6-C_3-C_2 = 114$

$C_6-C_3-C_1' = 131$

$C_7-C_4-C_3 = 126$

$C_8-C_4-C_3 = 125$

$C_4-C_3-C_1-C_2 = 144$

Figure 4. Geometry of the transition state for the rearrangement 1→2. Bond lengths are in Å and angles in degrees.
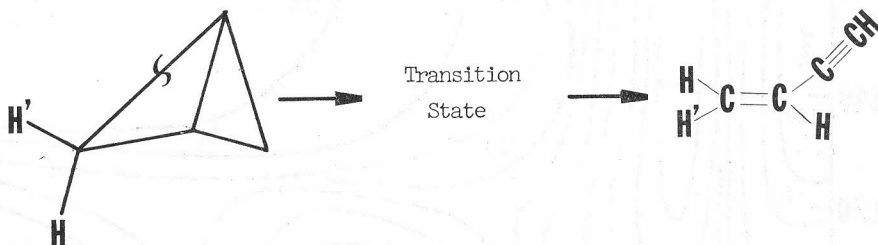

Figure 5. Depiction for the stereospecificity of the rearrangement 1→2.

It is interesting to note that the transition state geometry for **1 → 2** and that for cyclobutenylidene → **2**[10] are quite similar and, hence, have comparable ΔH_f values. For easy comparison, the geometry of the transition state for the latter process is shown in Figure 6. Thus it may be concluded that the post-transition-state paths for these two rearrangements are quite similar to each other.

Attention is now turned to the second rearrangement studied in this work: **1 → 3**; the energy contour map for the process is shown in Figure 7. The results indicate that the optimum path does not proceed via a direct C—H insertion. Instead, a biradical-like intermediate, **6**, which has an electronic structure (such as HOMO and LUMO symmetries) similar to that of **3**, is formed. The optimized geometry of **6** is shown in Figure 8.
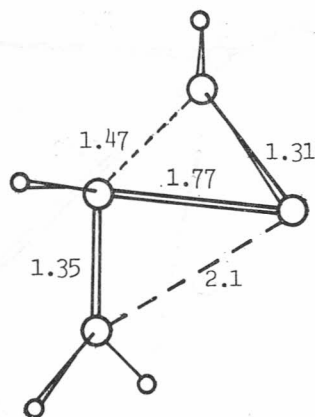
$\Delta H_f = 121$ kcal/mol

Figure 6. Geometry of the transition state for the rearrangement cyclobutenylidene $\rightarrow 2$[10]. Only the bond lengths (in Å) are shown.
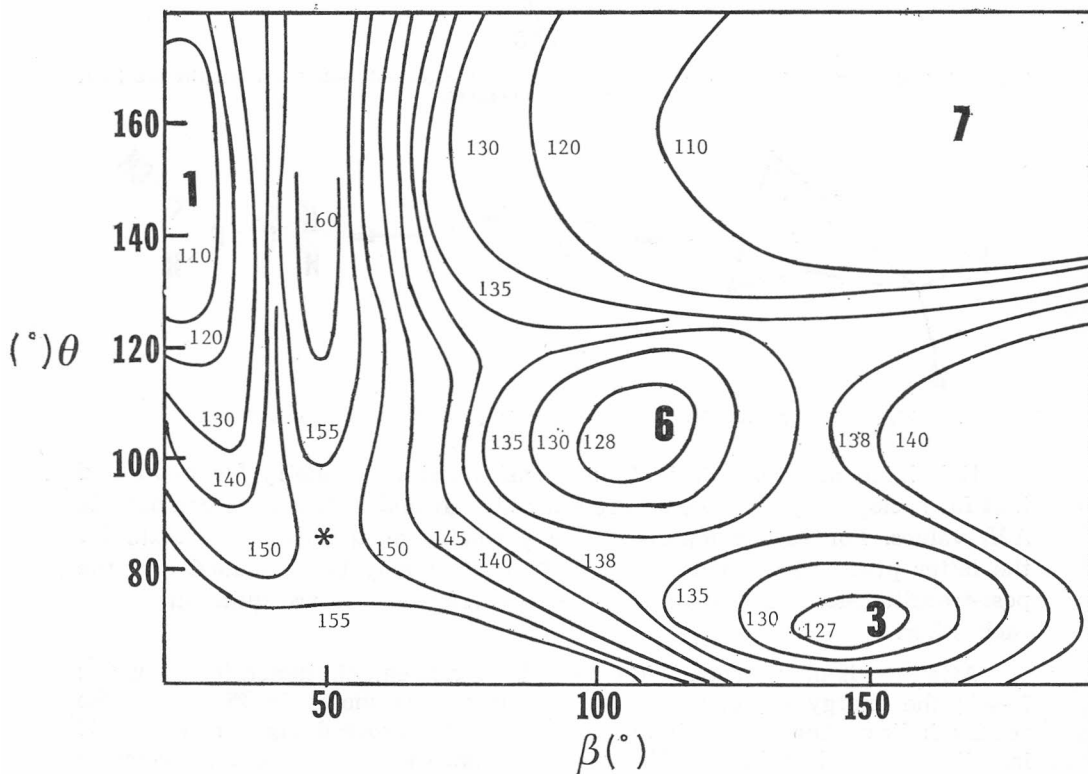

Figure 7. Energy contour map for the rearrangement 1→3. Contours are labelled in kcal/mol. The asterisk denotes the transition state, the geometry of which is chown in Figure 9.
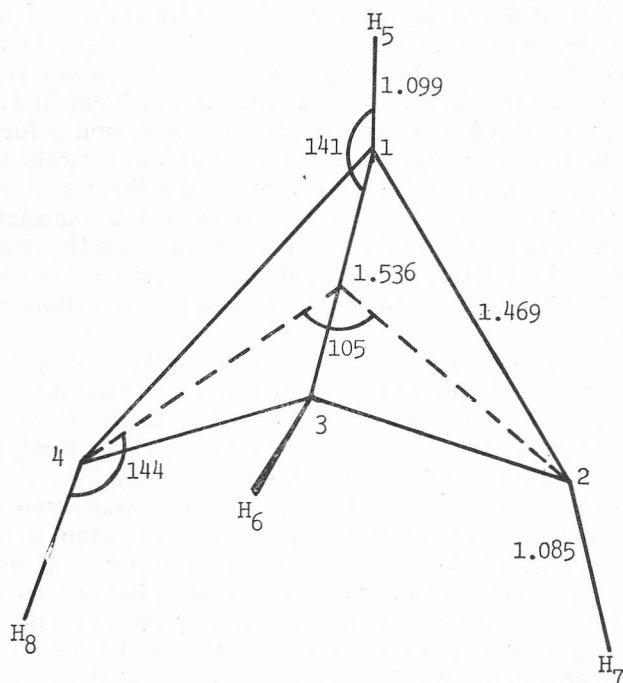
Fogure 8. Geometry of the biradical-like intermediate, **6**, found in the rearrangement **1→3**. The optimized structure has C_{2v} symmetry. Bond lengths are in Å and angles in degrees.
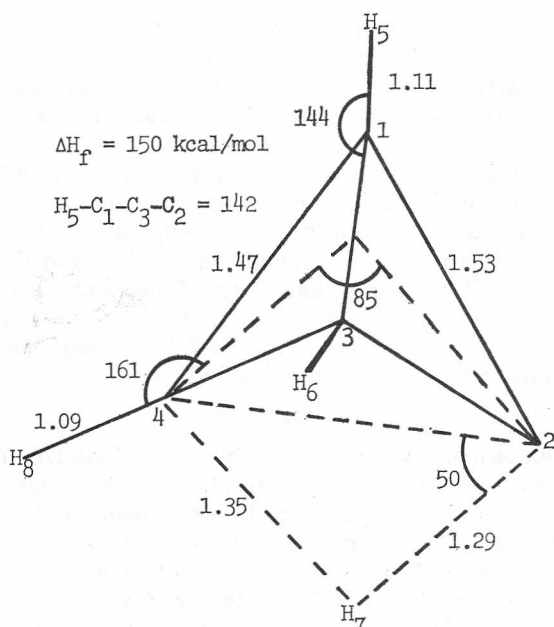
Fegure 9. Geometry of the transition state for the rearrangement **1→3**. Bond lengths are in Å and angles in degrees.

The formation of **6** can be interpreted as follows. At an early stage of the reaction, a decrease in Θ and an increase in β result in a decrease in C_2—H_7 distance (Figure 1). The structure of the transition state presented in Figure 9 indicates the formation of a three-center bond. It is obvious that the strain energy involved in such a structure is high and a further decrease in Θ (leading to the formation of **3**) causes still more strain such that the stabilization energy gained by the formation of the three-center bond cannot compensate for it. As a result, an increase in Θ with a concomitant increase in β, i. e., formation of **6**, release the strain after the transition state is reached. In other words, the MINDO/3 potential anergy surface predicts that the rearrangement **1** → **3** is accomplished via a two-step (abstraction-recombination) path: **1** → **6** → **3**.

As can be seen from Figure 7, it costs littl ein energy to move away from the aforementioned optimum path so that the formation of **3** from **1** via a direction C—H insertion is possible. According to the study of Hoffmann et al.[11] for the insertion of singlet methylene into a C—H bond, the transition state has a nearly linear configuration for C—H . . . (carbene)C. Since such a configuration cannot be obtained in the present intramolecular case, it is not surprising that the direct insertion or the two-step path requires a high activation energy of about 50 kcal/mol. In addition, **1** is predicted to be a polyene-like carbene (**5**) and the carbenic center is hence nucleophilic rather than electrophilic. The conclusion that **1** → **3** may or may not involve intermediate **6** is in agreement with Kollmar's study[12] of the insertion reaction of singlet cyclopropenylidene, which, like **1**, has a nucleophilic carbenic center. Kollmar has found that a non-concerted path with a radical intermediate may compete with the concerted process, with the latter also requiring a high activation energy, 41 kcal/mol.

Whatever the reaction mechanism (concerted or two-step) for **1** → **3**, the calculated heat of reaction and activation energy are 26 and 50 kcal/mol, respectively. Thus MINDO/3 predicts that both heat of reaction and energy of activation favor the rearrangement **1** → **2** over **1** → **3**, as found experimentally[3,4].

Finally, it should be mentioned that a minimum, **7**, which corresponds to a distorted cyclobutadiene molecule, appears on the upper right-hand corner of Figure 7. According to previous studies[13,14], the conversion of **3** into **7**, assuming C_{2v} symmetry, is thermally forbidden and does not involve **6**. In the present study, it is found that **6** and **7** are lumomers[15] and they are separated by an energy ridge as shown in Figure 7. The existence of such a ridge suggests[16] that the rearrangement **3** → **7** is accomplished without going through **6**, as results[13,14] of other workers indicate.

CONCLUSION

MINDO/3 calculations appear to be able to rationalize the observed formation of vinylacetylenes as the major products in the rearrangements of **1**[4]. In addition, it is found that the process **1** → **2** is concerted and stereospecific.

On the other hand, for the rearrangement of **1** → **3**, there is competition between the concerted and non-concerted (involving a biradical-like intermediate) paths, with the latter being slightly favored. Also, due to steric effects both paths are highly energetic, with activation energy being about 50 kcal/mol.

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SAŽETAK

MINDO/3 istraživanje termičkog pregrađivanja biciklobutanilidena

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Tri su mehanizma pregrađivanja biciklobutanilidena studirana pomoću MINDO/3 metode. To su slijedeći:
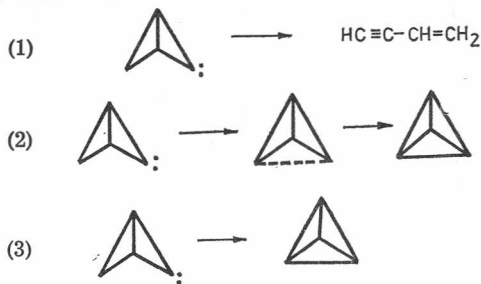
Teorijski račun daje prednost mehanizmu (1), koji je usklađen i stereospecifičan, prema mehanizmima (2) i (3). Taj je rezultat u slaganju s eksperimentalnim opažanjima. Mehanizmi (2) i (3) zahtjevaju veliku aktivacijsku energiju (oko 50 kcal/mol) zbog nepovoljnih steričkih efekata.

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