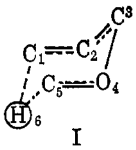


I

Viola and coworkers[23] have also proposed a completely planar transition state for the related thermolysis of β-hydroxyacetylenes. This reaction has also been previously shown[11] to have a symmetrical transition state by application of the full kinetic deuterium isotope criterion. It bears the same resemblance to β-hydroxyolefin thermolysis as has been identified here for the analogous reactions of benzyl allyl and benzyl propargyl ethers. The postulation[23] of two different transition states for β-hydroxyolefin and β-hydroxyacetylene thermolysis implies that the observed similarity of the activation parameters of these reactions is purely coincidental. It has been demonstrated in a previous article[1] that the near identity of activation parameters of benzyl allyl and benzyl propargyl ether thermolysis is not believed to be a mere coincidence.

A further reason for rejecting this as a coincidence of transition-state properties is based on the evidence afforded through application of the full kinetic deuterium isotope criterion. The identity of the isotope effect dependence on temperature, taken together with the striking similarity of activation parameters for allylic and propargylic ether (as well as for β-hydroxyolefins and β-hydroxyacetylene), thermolysis constitutes the most persuasive argument favoring a commonly structured transition state for all of these reactions. The constraint imposed by the ground-state geometry of the acetylenic bonding is clearly of no decisive consequence in the transition state of the retro-ene reaction.[1,20,24] This can be seen by comparing the ground state C–C–C distances (2.67 Å in acetylenes *vs.* 2.46 Å in olefins) and noting that the bending of the C–C–C framework in acetylenes requires surprisingly little energy (0.3 kcal for a 6° bend[23,25]). Thus, it is a matter of high likelihood that in a transition state some 40 kcal/mol above ground acetylenic substrates can assume the same geometry as their olefinic analogs. The considerations discussed above provide a reasonable (experimental) basis for the conclusion that this likelihood is realized in a number of reactions possessing a cyclic, symmetrical, transition state. Figure 2 appears to be an attractive way of portraying the molecular orbitals involved in such pericyclic processes of bond making and breaking.

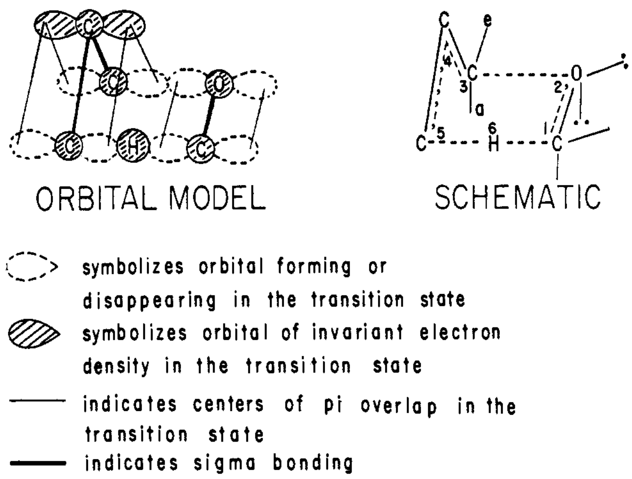


Figure 2. Transition state structure.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

(24) O. Achmatowicz, Jr., and B. Szechner, *J. Org. Chem.*, 37, 964 (1972).

(25) H. G. Viehe, "Chemistry of Acetylenes," Marcel Dekker, New York, N. Y., 1969, Chapter 1.

Ground States of Molecules. XXIV.[1] MINDO/2 Study of Some Reactions of Cyclopropylidene[2]

Nicolae Bodor,[3] Michael J. S. Dewar,* and Zvonimir B. Maksic[3,4]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received November 6, 1972*

Abstract: MINDO/2 calculations are reported for the rearrangements of singlet cyclopropylidene (carbenacyclopropane) to allene and to cyclopropene and for its addition to ethylene. The results account well for its observed behavior.

The reactions of atomic carbon with olefins have been studied in some detail by Skell and Engel.[5] In the case of singlet carbon, the product first formed is a singlet state of a cyclopropylidene (**1**). If the reacting carbon atom is in the excited ^1S singlet state, the cyclopropylidene rearranges immediately to an allene (**2**). If, however, it is in the lowest (^1D) singlet state, the cyclopropylidene does not rearrange in this way. In-

---

(1) Part XXIII: M. J. S. Dewar and P. Weiner, *Theor. Chim. Acta*, in press.

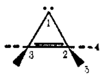
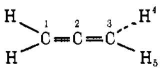
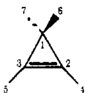
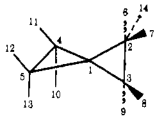
(2) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126.

(3) Robert A. Welch Postdoctoral Fellow.

(4) On leave of absence from the Rudjer Bosković Institute, Zagreb, Croatia, Yugoslavia.

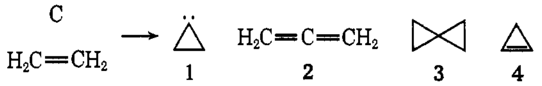
(5) P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 1135 (1965); **89**, 2912 (1967).

Table I. Theoretical and Experimental Geometries for S_0 Cyclopropylidene, Allene, Cyclopropene, and Spiropentane

Compd	Bond lengths, Å	Bond angles, deg	Dihedral angles,[a] deg
	$\overline{12} = 1.428$ $\overline{23} = 1.484$ $\overline{24} = 1.105$	$\overline{213} = 62.6$ $\overline{124} = 119.7$	$\overline{3124} = 250.5$ $\overline{3125} = 110.2$
	$\overline{12} = \overline{23} = 1.291$ (1.308)[b] $\overline{34} = \overline{35} = 1.093$ (1.087)	$\overline{234} = 123.3\ (118.2)$	$\overline{7134} = 90$
	$\overline{12} = 1.453\ (1.515)$[c] $\overline{23} = 1.300\ (1.300)$ $\overline{24} = 1.079\ (1.070)$ $\overline{16} = 1.112\ (1.087)$	$\overline{617} = 107\ (114°\ 42')$ $\overline{324} = 152.6\ (149°\ 55')$	
	$\overline{12} = \overline{15} = 1.475$ $\overline{23} = \overline{45} = 1.467$ $\overline{26} = \overline{27} = 1.106$	$\overline{627} = 106$ $\overline{1214} = 151.2$[d]	

[a] Dihedral angle $\overline{ijkl}$ is defined as the angular displacement of the $\overline{kl}$ distance relative to the $\overline{ij}$ one measured anticlockwise along the direction $j \rightarrow k$. In spiropentane, 14 is a point lying on the bisector of angle $\overline{627}$. [b] A. G. Malsi and R. A. Toth, *J. Mol. Spectrosc.*, **17**, 136 (1965). [c] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. G. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). [d] 14 and 15 are dummy atoms; $\overline{214}$ and $\overline{515}$ are bisecting the corresponding $\overline{HCH}$ angles.

stead, it reacts with a second molecule of olefin to form a spiropentane (**3**) together with other unidentified products.



1 **2** **3** **4**

In a preliminary communication,[6] Dewar, Haselbach, and Shanshal reported a study of the rearrangement of cyclopropylidene (**1**) to allene using MINDO/2.[7] They found a very high activation energy (~50 kcal/mol) for this process, a surprising conclusion since ^1S carbon reacts with olefins even at $-190°$ to form allenes. While a reasonable explanation of this apparent discrepancy was given, it seemed not unlikely that the calculated energies might have been in error due to the use of an early[7a] version of MINDO/2 and a rather crude procedure for calculating geometries. Since, moreover, no other calculations seem to have been reported for this reaction, the conversion of **1** to **3** or to cyclopropene (**4**), we thought it would be of interest to study these reactions using the later[7b] version of MINDO/2.

We have recently shown[8] that this procedure[7b] gives good estimates of the heats of formation and geometries of singlet (S_0, S_1) and triplet (T_1) carbene and also a good account of their insertion and addition reactions with methane and ethylene. We have also successfully used[9] MINDO/2 to study the structures of methylcarbene, formylcarbene, and cyclohexylidene, and also the course of their rearrangements into ethylene, ketene, and cyclohexene, respectively. It therefore seemed likely that useful information could be obtained in this way concerning the properties of **1**.

Procedure

The calculations were carried out by the standard MINDO/2 method,[7] using the parameters of part X.[7b] Geometries were calculated by minimizing the total energy with respect to all geometrical variables, using the Simplex method.[10] Minimum energy reaction paths were found by the procedure used in earlier papers of this series, *i.e.*, by choosing as reaction coordinate some parameter which varies monotonically during the reaction and, for various values of the reaction coordinate, minimizing the energy with respect to the other variables. A plot of energy against the reaction coordinate should then represent a section through the potential surface, along the lowest points in the valley linking the reactants to the products.

Results

Calculations were first carried out for the closed shell singlet (S_0) state of cyclopropylidene (**1**) and for allene (**2**), spiropentane (**3**), and cyclopropene (**4**). The results are compared with experiment in Table I.

In calculating reaction paths for the conversion of **1** to **2**, **3**, or **4**, various simplifying assumptions were made in order to reduce the amount of computation. These assumptions not only seem reasonable but are also supported by the results of earlier calculations[8,9] for the analogous reactions of other carbenes. They are indicated in Table II, together with the reaction coordinates used in the calculations of reaction paths.

Figure 1 shows plots of energy against the appropriate reaction coordinate for the conversion of singlet **1** to **2**, **3**, and **4** respectively. The activation energies deduced from these plots are as follows.

$$\mathbf{1} \rightarrow \mathbf{2} \qquad \Delta E^{\ddagger} = 13.7 \text{ kcal/mol} \qquad (1)$$

$$\mathbf{1} + C_2H_4 \rightarrow \mathbf{3} \qquad \Delta E^{\ddagger} = 5.8 \text{ kcal/mol} \qquad (2)$$

$$\mathbf{1} \rightarrow \mathbf{4} \qquad \Delta E^{\ddagger} = 6.3 \text{ kcal/mol} \qquad (3)$$

---

(6) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *J. Amer. Chem. Soc.*, **92**, 3505 (1970).

(7) (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

(8) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Amer. Chem. Soc.*, **94**, 9095 (1972).

(9) N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9103 (1972).

(10) See A. Brown, M. J. S. Dewar, and W. W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970).

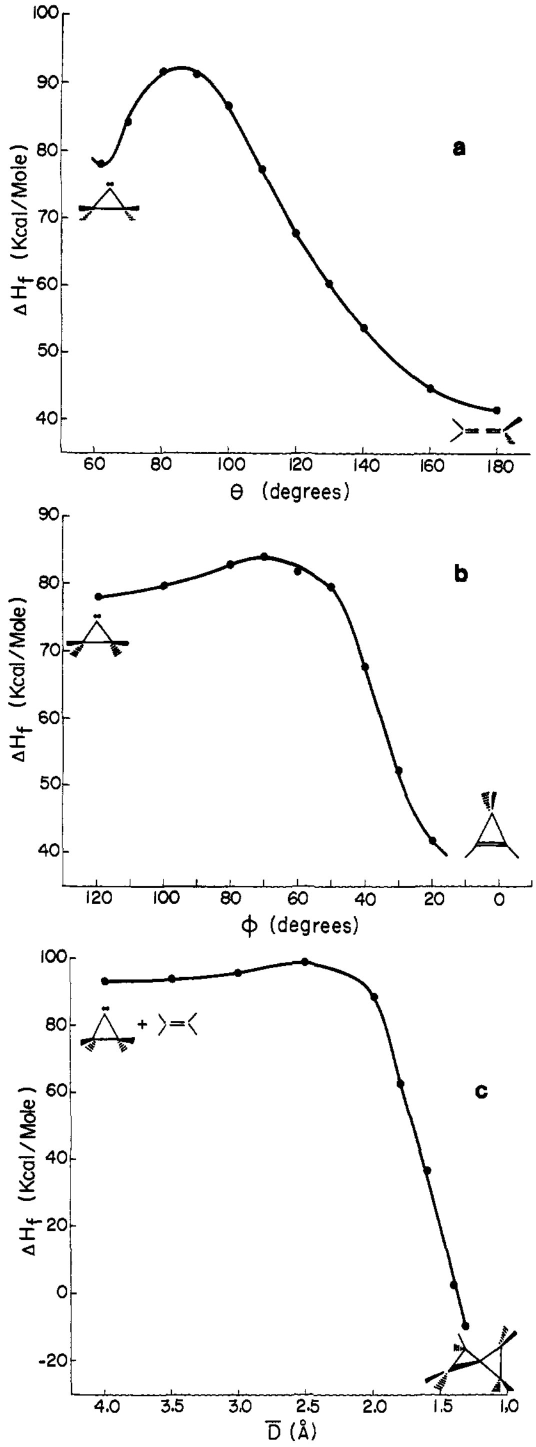


Figure 1. Plots of calculated heats of formation (ΔH_f, kcal/mol) *vs.* reaction coordinates (Table II) for reactions of singlet **1**: (a) ΔH_f *vs.* θ for **1** → **2**; ΔH_f *vs.* D for **1** + C_2H_4 → **3**; (c) ΔH_f *vs.* ϕ for **1** → **4**.

Figure 2 shows the calculated minimum energy path for approach of singlet **1** to ethylene to form **3**. C_s symmetry is retained throughout. The carbon atoms of the ethylene, and the carbenoid carbon atom, lie in the plane of symmetry which bisects the line joining the other two carbon atoms. Figure 2 represents successive projections of the system in this plane, the open circles representing the superimposed projections of the methylene carbons of **1** and the dots that of the carbenoid carbon.

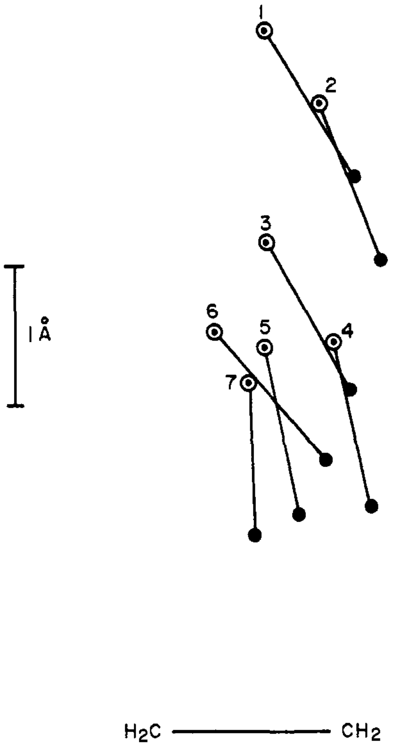
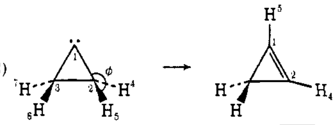
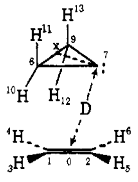


Figure 2. Successive stages (1–7) in the reaction of **1** with ethylene to form **3**. The open circles represent successive positions of the methylene carbons of **1** and the dots corresponding positions of the carbenoid carbon.

Table II. Reaction Coordination and Symmetry Conditions for the Reactions of S_0 Cyclopropylidene

Reaction and reaction coordinate	Symmetry conditions[a] during optimization
(1)  → **2** reaction coordinate: θ	All C–H bond lengths and $\overline{CCH}$ bond angles are equivalent
(2)  reaction coordinate: ϕ (= $\overline{125}$)	$\overline{36} = \overline{37}$ (C–H bond lengths not directly involved in the migration
(3)  reaction coordinate: D[b]	$\overline{13} = \overline{14}$ $\overline{25} = \overline{26}$ $\overline{8\ 10} = \overline{8\ 11} = \overline{9\ 12}$ $= \overline{9\ 13}$ $\overline{7\ 8} = \overline{7\ 9}$ $= 7811 = 7912$ $- 7913$ $213 = 214$ $125 = 126$

[a] All other geometrical parameters are variables. [b] D is the distance between point 0 (bisecting bond $\overline{12}$)and carbon 7. Angles 207 and 07X, as well as dihedral angle $\overline{107X}$, were variables.

Discussion

The calculated geometries (Table I) for **2**, **3**, and **4** are in reasonable agreement with experiment. The only serious discrepancy is in the case of cyclopropene where the calculated lengths of the single bonds are too large. The experimental value is close to that for sp^3–sp^2 C–C

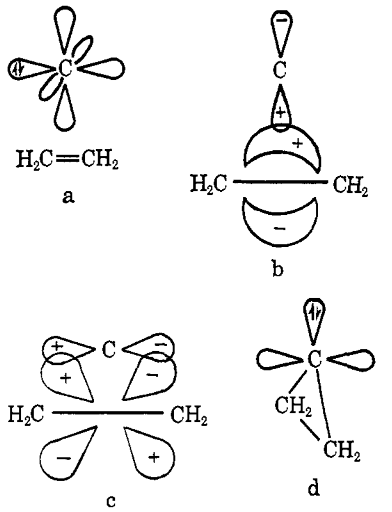


Figure 3. (a) Approach of a ^{1}D carbon atom to ethylene; (b) dative bond formation by interaction of the bonding electrons of ethylene with an empty 2p AO of carbon; (c) back-coordination by interaction of the filled 2p AO of carbon with the empty antibonding π MO of ethylene; (d) the filled orbitals of **1** in its S$_0$ state are symmetrical for reflection in the plane passing through the carbon nuclei.

bonds in unstrained systems (*e.g.*, 1.501 Å in propene[11]). This seems surprising, given that the length of the CC bonds in cyclopropane (1.510 Å)[12] is less than that of sp^3–sp^3 C–C bonds (1.53–1.54 Å) in paraffins. It might be added that *ab initio* SCF calculations[13] also predict a smaller value (1.493 Å) for the C–C bond length in cyclopropene than that observed and that both they, and MINDO/2, correctly predict the shortening of the CC bonds in cyclopropane.

The heat of formation calculated for **2** is also in good agreement with experiment but those for **3** and **4** are much too negative. This reflects the known[7] tendency of MINDO/2 to underestimate strain energies in three-membered rings. Since a similar error probably occurs in the case of **1**, we may expect our calculated heats of reaction to be too positive for **1** → **2**, too negative for **1** → **3**, and about right for **1** → **4**. The calculated activation energy for **1** → **2** should then be too large, for **1** → **3** too small, and for **1** → **4** more or less correct.

The reactions are, however, all extremely exothermic, each of them leading to an increase by one in the number of bonds. The calculated activation energies are also small. The kind of analysis introduced by Evans and Polanyi[14] then indicates[15] that the activation energies should be relatively insensitive to changes in the heats of reaction. One may therefore expect the errors in the calculated activation energies of eq 1–3 to be small compared with those in the calculated heats of reaction. Our calculations lead then to the prediction that singlet **1**, in the ground state (S$_0$), should undergo conversion more easily to **3** or **4** than to **2**.

^{1}D carbon has a closed-shell-type structure, one 2p AO being doubly occupied and the other two empty.

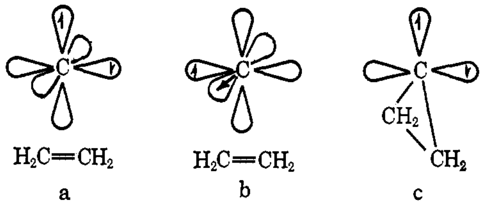


Figure 4. (a) Approach of a ^{1}S carbon atom to ethylene such that the overall wave function is symmetric with respect to reflection in the C$_3$ plane; (b) analogous approach in which the overall wave function is antisymmetric; (c) orbital occupation in the excited singlet (S$_1$) state of **1**.

In the approach of ^{1}D carbon to ethylene to form **1**, the optimum arrangement of orbitals will be as indicated in Figure 3a. The reaction is a typical π-complex process,[16] a dative bond being formed by interaction of the filled bonding π MO of ethylene with an empty 2p AO of carbon and a reverse dative bond by interaction of the filled 2p AO of carbon with the empty antibonding π MO of ethylene (see Figure 3b,c). The orbitals involved in the reaction are all symmetric with respect to reflection in the plane passing through the carbon atoms. The reaction can therefore lead directly to the lowest (S$_0$) singlet state of **1** whose wave function is symmetric for reflection in the place of symmetry containing the carbon nuclei (Figure 3d).

The situation is, however, quite different in the case of ^{1}S carbon. In ^{1}S carbon, two 2p AO's are singly occupied while the third is empty.[17] When a ^{1}S carbon atom approaches ethylene, the wave function of the system can be symmetric with respect to reflection in the C$_3$ plane only if the approach is as indicated in Figure 4a. This approach, however, is unfavorable because it would involve an interaction between the filled bonding π MO of ethylene and a singly occupied AO of carbon. One electron would then be forced into an antibonding MO.[16] The resulting structure would be analogous to a π complex formed by a radical instead of a cation. Such π complexes are relatively unstable[16] because of the enforced promotion of a nonbonding electron into an antibonding MO. The preferred mode of approach will therefore be that indicated in Figure 4b. Here the bonding π MO of the ethylene interacts with the empty carbon 2p AO. However, one carbon electron now occupies a 2p AO which is antisymmetric with respect to reflection in the C$_3$ plane. The wave function of the system (C_3H_4 + C_2H_4) is then likewise antisymmetric. Reaction will therefore tend to lead to a correspondingly antisymmetric state of **1**, *i.e.*, the S$_1$ state of Figure 4c where the two carbenoid AO's are each singly occupied. This symmetry requirement will then lead to the formation of singlet **1** in its excited (S$_1$) state rather than the ground state (S$_0$).

Criticisms have been leveled[18] against arguments

---

(11) D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

(12) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).

(13) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).

(14) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1340 (1936).

(15) See M. J. S. Dewar, *Discuss. Faraday Soc.*, **2**, 261 (1947).

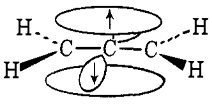
(16) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951); "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949; "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(17) In the case of an isolated carbon atom, the ^{1}S state cannot be represented by a single Slater determinant. Such a wave function would not be an eigenfunction of the operator M^2. In the present situation, however, the central symmetry of the field in which the electrons move is destroyed by the neighboring ethylene molecule. Here the angular momentum is no longer a constant of the motion so that states of the carbon atom can be represented in terms of individual configurations constructed from real 2p AO's.

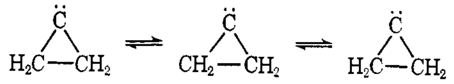
(18) See M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971); *Angew Chem., Int. Ed. Engl.*, **10**, 761 (1971).

based on the conservation of symmetry of wave functions during reactions[19] on the grounds that chemical reactions rarely can, and never need to, involve the retention of symmetry during their intermediate phases. This, however, is a rather exceptional case. Orbital overlap will strongly tend to constrain the reacting carbon atom to approach ethylene in the plane bisecting the ethylenic HCH groups. Under these conditions, orbitals which are antisymmetric with respect to reflection in that plane will have very little tendency to mix with symmetric ones. There will therefore be a very high probability that the reaction of ^{1}S carbon with ethylene will yield **1** in the excited S_1 state.

Our MINDO/2 calculations predict the S_1 state of **1** to lie 15 kcal/mol above the S_0 state. It is also easily seen that this separation should decrease with an increase in the apical angle (*i.e.*, $C\ddot{C}C$) of **1**. Thus increasing this angle to 180° without rotation of the methylene groups would lead to a planar rotamer (**5**) of **2**. Here there are two NBMO's, *i.e.*, an AO of the central carbon atom and an allylic NBMO. The S_0 and S_1 states are then orbitally degenerate. There should therefore be a strong coupling between the $S_0 \rightarrow S_1$ electronic transition and the normal mode of vibration of the three-membered ring of **1** indicated in **6**. The electronic excitation in S_1 **1** should therefore be very much available for internal conversion to precisely the vibrational mode needed to transform **1** to **2**. This excitation energy is greater than our estimate of the activation energy required for this rearrangement. Furthermore, the ^{1}S state of carbon lies 33 kcal/mol above the ^{1}D state. The reaction with ethylene to form **1** will be correspondingly more exothermic. The excess energy will go into vibrational energy of **1** and, as has been previously pointed out,[6] a large part of this vibronic energy should again go into the normal mode of vibration indicated in **6**. It is therefore not at all surprising that the reaction of ^{1}S carbon atoms with olefins leads exclusively to allenes.[5]



5



6

On the other hand, the reaction of a ^{1}D carbon atom with ethylene is both less energetic and can, and should, lead to the lowest (S_0) singlet state of **1**. Here it is very likely that there will be initially insufficient vibrational energy in the normal mode of **6** for immediate conversion to **2**. In this case the excess vibronic energy will be lost, leaving **1** in its lowest singlet state (S_0). Our calculations then imply that rearrangement to cyclopropene (**4**) and reaction with ethylene to form spiropentane (**3**) should both occur more easily than rearrangement to allene (**2**). This of course is entirely consistent with the results reported by Skell and Engel.[5] The products from ^{1}D carbon atoms and olefins contain no allenes, consisting of a mixture of spiropentanes and unidentified products. If we are right in our prediction that rearrangement of **1** to **4** should be as facile as addition of **1** to olefin, complex products might be expected from secondary reactions of the resulting cyclopropenes.

(19) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965); R. Hoffman and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

Thermal Rearrangements of Methylenecyclobutanes. Kinetics of Equilibration of (*E*)- and (*Z*)-1-Ethylidene-2-methylcyclobutane and *cis*- and *trans*-1-Methylene-2,4-dimethylcyclobutane[1]

John E. Baldwin* and Ronald H. Fleming[2]

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403. *Received February 12, 1973*

Abstract: The isomeric methylenecyclobutane systems (*E*)- and (*Z*)-1-ethylidene-2-methylcyclobutane and *cis*- and *trans*-1-methylene-2,4-dimethylcyclobutane have been synthesized, identified, and thermally equilibrated at 332°. The two 1-(1-deuterioethylidene)-2-methylcyclobutanes have been prepared and equilibrated with the corresponding 1-ethylidene-2-deuterio-2-methylcyclobutanes. The rate constants obtained reveal some striking stereochemical effects. The 1-methylene-2,4-dimethylcyclobutanes rearrange preferentially to the *E* isomer of 1-ethylidene-2-methylcyclobutane. The *Z* isomer of 1-ethylidene-2-methylcyclobutane isomerizes with predominant cleavage of the more substituted C(2)–C(3) bond, but the *E* isomer does the opposite—the C(3)–C(4) bond is preferentially broken. Both *E* and *Z* isomers show net retention of geometrical configuration about the ethylidene unit during 1,3-carbon migration originating from C(2).

Kinetic studies on the gas phase unimolecular cycloreversion of methylenecyclobutane (**1**) to ethylene and allene[3–6] and on the conversion of spiropentane (**2**) to both methylenecyclobutane and the ethylene–allene

(1) Supported by the National Science Foundation and Hoffmann-La Roche Inc.

(2) National Science Foundation Predoctoral Trainee, 1968-1972.

(3) P. J. Burkhardt, Dissertation, University of Oregon, 1962.

(4) J. P. Chesick, *J. Phys. Chem.*, **65**, 2170 (1961).

(5) R. L. Brandaur, B. Short, and S. M. E. Kellner, *ibid.*, **65**, 2269 (1961).

(6) W. J. Engelbrecht and M. J. DeVries, *J. S. Afr. Chem. Inst.*, **23**, 163, 172 (1970).