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The Role of 2,3-Dimethylene-1, 4-cyclohexadiyl Diradical as a Reactive Intermediate in Some Rearrangement Reactions

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Quantum chemical CI calculations with the semiempirical MO method SINDO1 are performed to study the rearrangement reactions of 1,2,6,7-octatetraen, 2,3-dimethylenebicyclo(2.2.0)hexane, 3,4-dimethylene-1,5-hexadiene and bicyclo(4.2.0)octa-1,5-diene. It is shown that the most favorable pathway of each of these six rearrangements involves the 2,3-dimethylene-1,4-cyclohexadiyl diradical as an interceptable intermediate. Two further intermediates, 1,2-divinyl-1-cyclobutene and 1,2-divinylylcyclobutane appear, but the latter with little importance. Energies and geometries of the four reactants resp. products, the three intermediates and twelve transitions states are presented. The mechanism of the rearrangements is discussed.

Key words: Reactive intermediates – Rearrangement reactions.

1. Introduction

In organic chemistry, diradicals are often referred to as intermediates in chemical reactions. However, in most cases it is not quite clear whether these structures are real intermediates or just transition states. In the first case, they constitute minima on the potential hypersurface and can be intercepted, whereas in the second case they refer to saddle points without a finite lifetime. To establish a basis for further discussion we refer to the review by Salem and Rowland [1] for the definition of a diradical. A diradical is a structure for which the first singlet and triplet are degenerate or quasidegenerate. This means there is a degeneracy of the HOMO and LUMO which are both singly occupied with no

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preference for the orientation of the two spins. Vrom this definition it is clear that a diradical is not necessarily an extremum on the potential hypersurface but may refer to a whole region, i.e. a cut through the hypersurface on which the degeneracy is maintained. Interesting for the chemist are only those diradicals which are either stable molecules, intermediates or transition states. In two reviews Huisgen has dicussed the question how to stabilize an intermediate in the reaction of tetracyanoethylene and enol ethers [2] and how to intercept the intermediate in the ethylene dimerization [3]. We have contributed to the discussion of this problem by the calculation of the transition states and intermediates of the cycloreversion of unsubstituted and substituted cyclobutane [4]. Our results were based on CI calculations with the semiempirical MO method SINDO1 [5,6]. It was concluded that the diradical intermediate could not be intercepted in the gas phase, neither in the unpolar nor in the polar form, because the well depth was too small. Although the assumption that small minima exist on the tetramethylene potential surface has been substantiated by our calculations and for this reason the reaction has to be classified as non concerted, we were dissatisfied by the lack of experimental consequences. Since we found in another investigation on cycloreversion reactions for five to seven membered rings that the well depth may increase with ring size [7], we expected a better chance for an interceptable diradical intermediate in a larger system. For this purpose we selected the 2,3-dimethylene-1, 4-cyclohexadiyl diradical which had been extensively studied in the group of Roth [8–12], in the gas phas as well as in solution. We address ourselves to the gas phase results. These researchers found the above diradical as an intermediate in the reaction from such reactants as 1,2,6,7-octatetraene [9, 11–12] or 2,3-dimethylenebicyclo(2.2.0)hexane [8, 11–12] to products 3,4-dimethylene-1,5-hexadiene and bicyclo(4.2.0)octa-1,5-diene. In the following, we call this diradical I_1 and the reactants R_1, R_2 and products P_1, P_2. We wanted to study whether I_1 is a diradical in the sense of Salem [1] and what role it plays in the various rearrangement reactions of R_1, R_2, P_1, P_2.

2. Results and Discussion

To depict the situation we present the possible pathways and intermediates schematically in Fig. 1. We have enlarged the discussion by the inclusion of two further intermediates: 1,2-divinyl-1-cyclobutene (I_2) and 1,2-divinylylcyclobutane (I_3). Roth and coworkers addressed themselves mainly to the study of I_1 and the pathways T_1 and T_2, and a brief discussion of the conversion of P_1 to P_2 via I_2. They also studied the dimerization of I_1 which has been excluded from the present work becuase it would increase the number of reaction pathways substantially and also the computer time involved. Furthermore, as experiments show, dimerization becomes important only in solution, not in the gas phase. In solution the triplet state of I_1 is essential for the reaction, whereas in the gas phase the spin change is slower than the product formation on the singlet surface. Still we had four stable molecules, three intermediates and twelve transition states to study. We calculated the energy of minima and saddle points using SINDO1 [5, 6] with a 4×4 CI. All geometries were fully optimized with saddle

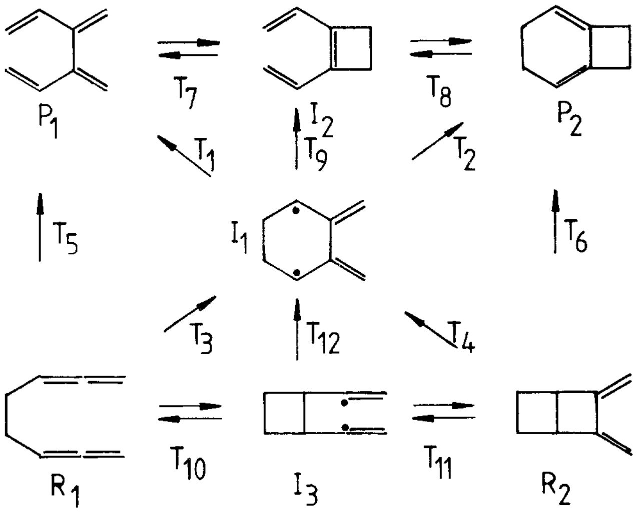

Fig. 1. Reaction scheme

points characterized by one negative eigenvalue of the force constant matrix. We have collected the relative energies, the singlet-triplet splitting and the dipole moments in Table 1. From this table it is apparent that the concerted pathways between the various reactants and products are forbidden. Allowed are the sequences $R_1 \to T_3 \to I_1 \to P_1$, $R_1 \to T_3 \to I_1 \to P_2$, $R_2 \to T_4 \to I_1 \to T_1 \to P_1$, $R_2 \to T_4 \to I_1 \to T_2 \to P_2$. So all feasible pathways are nonconcerted and involve the intermediate I_1. This diradical is stabilized by the two methylene groups. In the case of P_1 we found two conformers: the orthogonal C_2 symmetry form P_1 and the C_s symmetry form P_1'. The latter is only 1.1 kcal/mol higher in energy, but it cannot easily be reached from I_1 because of the substantially higher barrier of T_1' (35.7 kcal/mol) compared to T_1 (5.2 kcal/mol). From the calculation we would expect at low temperature equal portions of P_1 and P_2 when kinetic control dominates as is the case from R_1 produced from I_1 because the energies of T_1 and T_2 differ by less than 1 kcal/mol. But thermodynamic control favoring P_2 would shift the proportion to P_2 when the reactant is R_2, because the transition state T_4 has a substantially lower energy than T_3. The pressure dependence [8–12] of the ratio of P_1 to P_2 can be explained as follows. The higher barrier T_3 (65.4 kcal/mol) produces an excess energy in I_1 which at low pressures equilibrates the products. The lower barrier T_4 (59.3 kcal/mol) is not substantially higher than T_1 (55.4 kcal/mol) or T_2 (56.0 kcal/mol) and cannot produce the same effect. Increase of pressure deactivates intermediates and products and favors P_2 for enthalpy reasons. For higher temperatures, the entropy contribution to the free energy would favor P_1, because this product contains several degrees of freedom for internal rotation about single bonds which are missing in P_2.

This is in agreement with the findings by Jelich [12]. At high pressure he finds a ratio for P_1 to P_2 of 40:60 starting from R_2. At low pressure P_1 is the main product starting from R_1. At 250°C temperature P_2 is converted into P_1. However, he estimates the absolute values of the barriers of T_1 and T_2 as

Table 1. Relative energies E (kcal/mol), singlet-triplet splitting $\Delta E = E_T - E_S$ (kcal/mol) and dipole moments for extrema on the reaction potential surface

State	E	ΔE	D
R_1	31.1	—	1.05
R_2	31.8	—	0.73
$P_1\,(C_2)$	26.0	—	0.39
$P_1'\,(C_s)$	27.1	—	0.63
P_2	0	—	0.35
I_1	50.2	−0.2	0.96
I_2	20.1	100.6	0.26
I_3	74.1	1.3	1.92
$T_1\,(C_2)$	55.4	−0.0	0.71
$T_1'\,(C_s)$	76.9	75.0	0.86
T_2	56.0	5.8	0.73
T_3	65.4	−0.2	1.12
T_4	59.5	4.0	1.11
$T_5\,(C_2)$	88.8	6.3	0.14
$T_5'\,(C_s)$	88.2	8.3	0.65
T_6	92.0	−1.1	0.66
$T_7\,(C_2)$	77.5	11.5	0.21
$T_7'\,(C_s)$	79.5	0.1	0.62
T_8	75.2	−0.5	1.02
T_9	63.0	109.1	0.18
T_{10}	107.5	27.3	1.57
T_{11}	74.9	3.6	1.77
T_{12}	81.0	73.0	1.23

14–15 kcal/mol compared to our 5.4 and 6.0 kcal/mol. We did not find other diradicals like bicyclo(4.2.0) 1,6-octene-2,5-diyl as extrema on the potential surface. This excludes alternative nonconcerted pathways, well in agreement with experiment [8–12]. We consider now the pathways from P_1 to P_2 and R_1 to R_2. Next we consider the synchronous pathways from R_1 to P_1 and R_2 to P_2. Both are energetically unfavorable compared to the nonconcerted pathways via I_1. This is partially in disagreement with conclusion by Jelich [12] who claims that a competing synchronous pathway T_5 must exist to explain the shift of product ratio P_1 to P_2 in favor of P_1 when the reactant is R_1. We have explained above why this need not be so. The reaction from R_1 to P_1 can be considered as a Cope rearrangement. The simplest case, namely the 1,5-hexadiene rearrangement has been discussed by Dewar [13, 14]. He found intermediates analogous to I_1. The well was 1.6 kcal/mol for the boat form and 2.7 kcal/mol for the chair form. The latter was more stable by 6.3 kcal/mol. As we said before I_1 is stabilized by the two methylene groups. Its well depth, which may be underestimated by the 5.2 kcal/mol of our calculation, is apparently sufficient for interception. The interconversion of P_1 to P_2 via I_2 has a barrier of 77.5 ckal/mol. Interconversion should be feasible only at higher temperatures. The interconversion of R_1 to R_2 via I_3 is analogous to the ethylene dimerization and energetically forbidden, because it involves the Woodward-Hoffmann forbidden planar approach of two ethylene fragments. From our calculation it would seeem unlikely to intercept I_3 because of insufficient well depth.

Besides the question of the favorable reaction pathway it is improtant to know the amount of diradical character for each of the states. From Table 1 we conclude that I_1 is a diradical with the triplet state by 0.2 kcal/mol lower than the singlet state. This is in agreement with EPR measurements by Jelich [12]. Also diradicals are the transition states T_1 and T_3. In these cases and in T_6 the triplet is lower than the singlet. Almost degeneracy is found in T_7 with the singlet lower by 0.1 kcal/mol. In this category we can put also I_3 which was formally defined as a diradical. In the transition states T_2 and T_4 the singlet is already substantially lower than the triplet and in rest of the molecular states there is no appreciable diradical character either.

The dipole moments may be grouped into two categories: large dipole moments between 1 and 2 Debye for intermediates I_1 and I_3 and their adjacent transition states T_3, T_4, T_{10}, T_{11}, T_{12}, also R_1, T_8 and small dipole moments up to 1 Debye for the reactants, products and the rest of the intermediates and transition states.

The large dipole moment in I_1 stems mainly from the charge shift from the six membered ring to the outer carbons, whereas the main part of the dipole moment of I_3 is due to the polarization of the two radical centers from the localization of the radical electrons. In T_{10} there is a shift of charge from the inner to the outer carbons. The situation of T_{11} resembles the one in I_3. In T_{12} there is both a charge shift from the inner to the outer carbons and a hybridization of the radical centers of I_3. In T_1 there is a density and a hybrid component to the dipole mement. The first is due to charge alternation with the outer carbons and the radical centers of I_1 being negative and the other carbons being positive. The hybrid part comes from the radical centers of I_1 due to distortion from planarity of the six membered ring. A similar situation prevails in T_3.

The geometry of all states is presented in Fig. 2–6. Fig. 2 shows R_1 consisting of two allenes connected by a CC bond in a planar carbon framework. R_2 consists of two quadratic carbon rings with a dihedral angle of 121° between them. The intermediate I_1 has again a planar carbon framework. This is due to the presence of the two methylene groups and different from the plain 1,5-hexadiyl. The planar carbon framework is retained in the transition state T_3. The ring bond is not yet formed and the bond orders of two double bonds of the allene fragments are only slightly reduced. In T_4 the CC bond connecting the two rings of R_2 is broken, but the framework is still substantially nonplanar with a dihedral angle of 123°. Fig. 3 shows the pathways from I_1 to P_1 and P_2. P_1 has the C_2 symmetry of two orthogonal transbutadienes connected by a CC bond. P_2 has a planar carbon framework. In T_1 the dihedral angle between the two butadienes has been increased to 19° from 0° in I_1. The outer CC ring bond has been slightly reduced and the double bond character of the adjacent CC bonds begins to form. In T_2 bonds are similar to P_2. The two double bonds of I_1 are single bonds now. Fig. 4 shows a nonplanar I_2 with C_2 symmetry. In T_7 the four

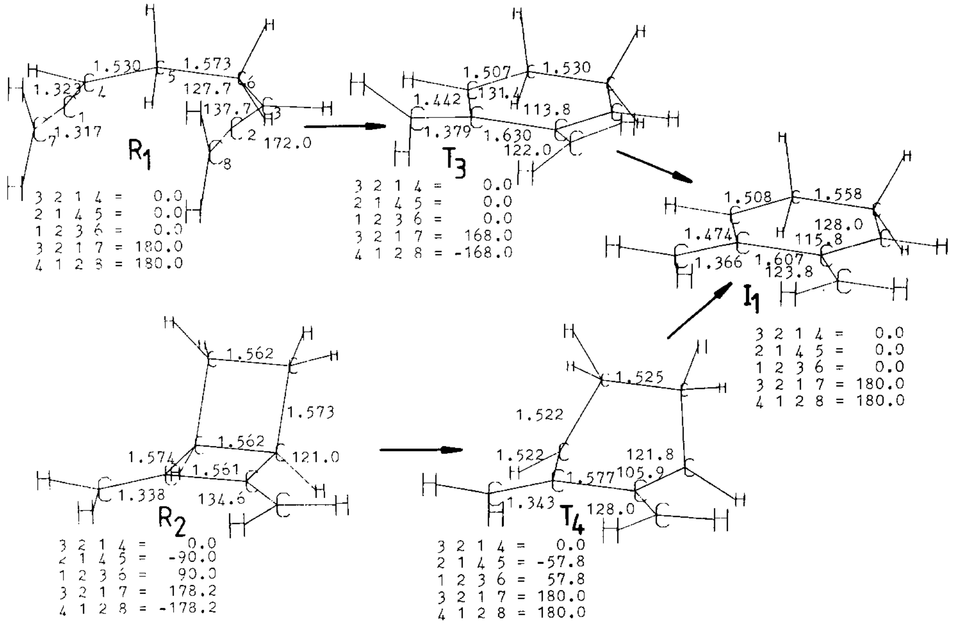

Fig. 2. Geometries of R_1, R_2, T_3, T_4, I_1

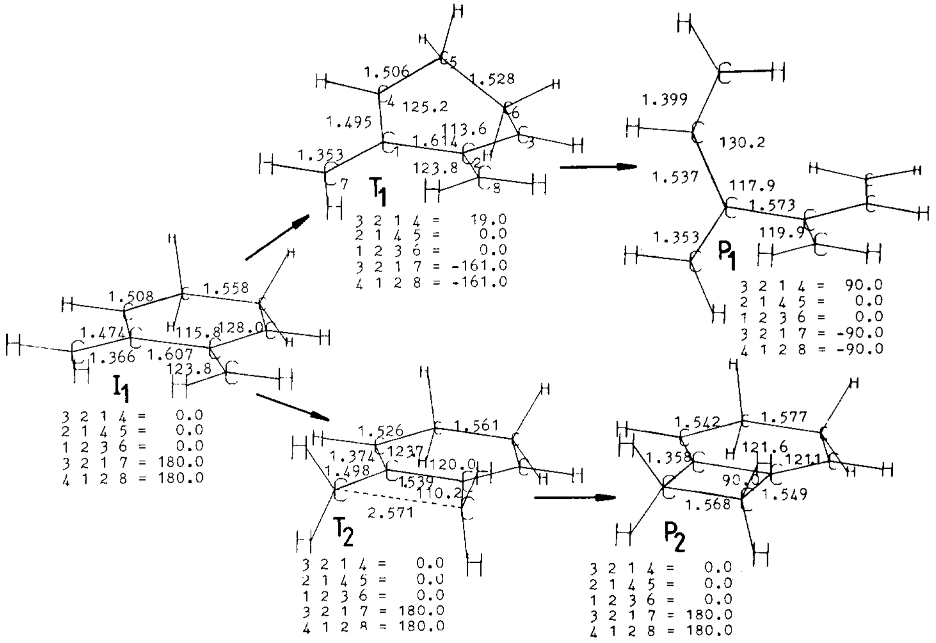

Fig. 3. Geometries of I_1, T_1, T_2, P_1, P_2

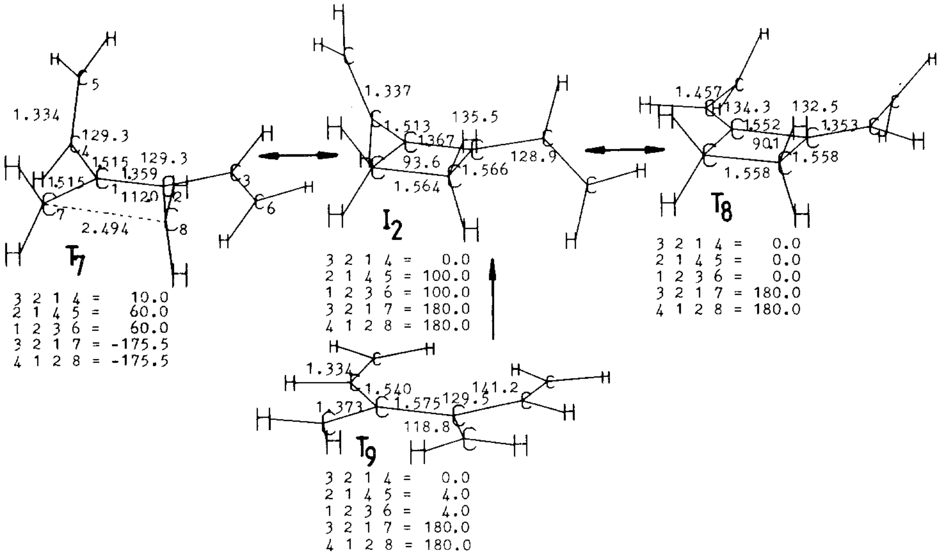

Fig. 4. Geometries of I_2, T_7, T_8, T_9

membered ring has been opened by substantial increase of its outer CC bond and accompanying increase of the bond order of the adjacent CC bond. T_8 resembles more I_2 than P_2. It is non-planar and the six membered ring has not yet been formed. In T_9 there is no ring bonding in the six membered ring and reduced bonding in the crucial CC bond of the four membered ring. The CC bond between the two rings has single bond character. Fig. 5 shows the situation of I_3 and its adjacent transition states. I_3 is substantially non-planar with dihedral angle of 124° between the plane of the four membered ring and the next carbon plane. The CCC angle of 145° of the four membered ring substituents shows substantial deviation from linearity (180°) and allows the localization of the radical electrons. In T_{10} the above dihedral angle has been increased to 129° far from 0° as in R_1, but the CC bond holding the four membered ring has been broken. The above mentioned CCC angle is increased to 158° and the allene moiety has already been formed. The geometry of T_{11} is similar to the one of I_3. T_{12} is highly non-planar with a dihedral angle of 78° compared to 57° in I_3 and 0° in I_1. The crucial four membered ring bond has been reduced. The bond length is 1.97 Å. The six membered ring bond is mostly formed with a CC bond length of 1.65 Å.

For completeness we present the remaining geometries in Fig. 6. T_5 resembles the weak interaction of two butadienes. T_6 is non planar with a dihedral angle of 132° between the two four membered rings of R_2, but the connecting CC bond is completely broken with a CC distance of 2.60 Å. There is however no formation of the four membered ring of P_2. The rest of the cases concern an alternative product P_1' of C_s symmetry and pathways leading toward its.

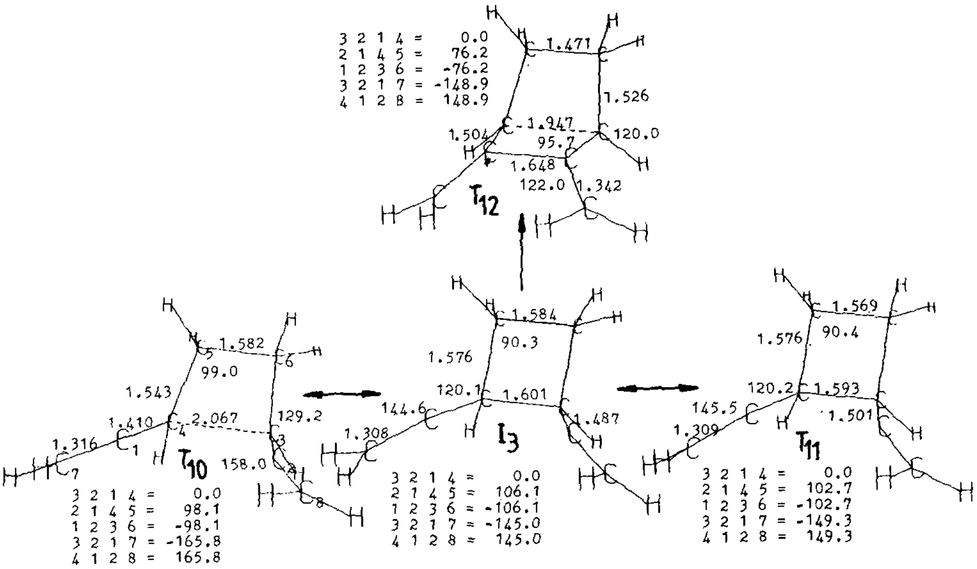

Fig. 5. Geometries of I_3, T_{10}, T_{11}, T_{12}

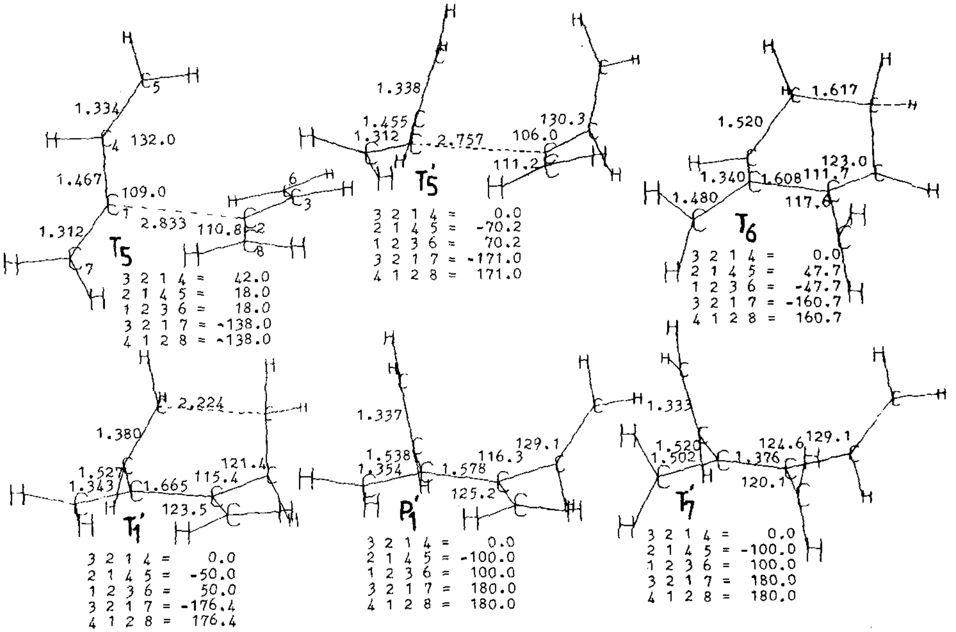

Fig. 6. Geometries of T_5, T_5', T_6, T_1', P_1', T_7'

3. Conclusion

The intermediate diradical I_1 plays a central role in the rearrangements considered here. It is stabilized by the two methylene groups. Its triplet is lower than the singlet by 0.2 kcal/mol. If we compare the direct concerted pathways of R_1 to P_1 and R_2 to P_2 via T_5 and T_6 with the diradical pathways via I_1, it is apparent that the concerted pathways involve more changes in the bonding structure than each of the diradical pathways via T_3, T_1 and T_4, T_2. The reaction will proceed therefore in a noncerted fashion. This argument is substantiated by calculations of transition state energies. The proposed mechanism of various rearrangements is in agreement with experiment. In particular changes of the ratio of products P_1 to P_2 which depend on temperature and pressure can be explained by the calculated data. The relative stability of P_1 and P_1' gives no clue on the feasibility of the pathways leading to the two conformers. Pathways involving intermediates I_2 and I_3 are less important. An easy interconversion of P_2 to P_1 seems not quite likely at low temperatures. In the gas phase, it seems safe to exclude the triplet state of I_1 or the existence of another diradical, such as bicyclo(4.2.0)1,6-octene-2,5-diyl, from the discussion of the reaction mechanism.

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