V. Conclusions and Summary

1. We have shown that structure sensitivity in dispersed metal catalysts is describable in terms of a simple scaling power law.

2. A single parameter, the reaction dimension D_R, allows quantitative evaluation of the degree of structure sensitivity and comparative evaluation of (unrelated) reactions and catalysts.

3. This tool is general and applicable to virtually all types of catalytic reactions as indicated in Table I.

4. A wide range of D_R values has been revealed: from close to 0 up to 6.

5. It is suggested that the observed D_R values originate from specific dependencies of the relative proportion of active surface atoms or sites on particle size. This hypothesis was tested by fitting three of the experimental D_R values to surface-atom statistics of suggested crystallite models. For experimental D_R = 0.71, 1.16,

2.77 the calculated D_R = 0.79, 1.18, 2.90 were obtained (Figures 6–8).

6. For crystallites with surface fractal dimension ~ 2, $D_R \leq$ 2 has been interpreted in terms of invariance of the pattern of distribution of active sites to scale transformation, i.e., that D_R reflects the fractal dimension of the subset of active sites out of all surface atoms. Pattern invariance does not hold for $D_R > 2$ (or more generally for $D_R > D$) values, but common to all D_R values is the scaling behavior: magnifying by a factor of N increases the number of relevant surface features to N^{D_R}.

The main purpose of this paper has been to report the phenomenon, its generality, and its potential applications and to suggest preliminary interpretations. In following publications we concentrate on specific families of heterogeneous catalytic reactions and on chemisorptions. For preliminary reports see ref 6a,d and 7d.

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SINDO1 Study of the Photochemical Reaction Mechanism of Di-π-methane

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Abstract: SINDO1 calculations on the configuration interaction (CI) level were performed in an investigation of the photochemical di-π-methane rearrangement. Several diradical intermediates and one transition structure were located on the lowest triplet potential surface. Correlation diagrams are presented for two alternative pathways to vinylcyclopropane. The diagrams confirm the general idea of the mechanistic pathway suggested by Zimmerman. The singlet mechanism is efficient if no barriers on the first excited singlets occur during the reaction. This is the case for central dimethyl substitution of the reactant. Here cyclopropyldicarbinyl is not an intermediate. The triplet mechanism can be efficient only if the cyclopropyldicarbinyl triplet intermediate is circumvented during the reaction so that back reaction to the reactant ground state is avoided.

I. Introduction

The di-π-methane rearrangement is a photochemical reaction that was discovered and the mechanism proposed by Zimmerman so that it is sometimes called the Zimmerman rearrangement. The experimental data and mechanistic scheme are lucidly described in a recent review.[1] According to the mechanism the unsubstituted di-π-methane undergoes a rearrangement to vinylcyclopropane after irradiation with light. In the mechanistic scheme (Figure 1) it is assumed that two diradicals are involved in the reaction which serve to establish a bridge bond between the two π bonds and subsequently break one of the two single CC bonds of the initially central carbon atom. Finally the two new diradical centers rearrange and form the three-membered ring. Zimmerman is cautious in pointing out that the two diradicals need not be energy minima on the potential surface. The symmetry of the simple scheme of Figure 1 is modified if substituents render the two π bonds unequivalent. According to Zimmerman acyclic di-π-methane reactants react effectively from their singlet excited states. This claim was supported by experimental evidence on

cis- and trans-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene,[2] where direct irradiation led to a normal di-π-methane rearrangement whereas sensitized irradiation, in which the reactant was in the triplet state, led to no di-π-methane rearrangement. It was shown that triplet excitation was diverted into a rotation about one of the acyclic π bonds. In the singlet rearrangement it should also be operative, but the rates of rotational relaxation are too slow compared with the rates of rearrangement.

To our knowledge no experimental data are available on the rearrangement of the parent di-π-methane compound in solution, but a few symmetrically substituted molecules were investigated. For 1,1,5,5-tetraphenyl-1,4-pentadiene a hydrogen migration mechanism was found to be operative with low product yield.[3] In other cases the central carbon atom had two methyl groups attached to itself. Here the mechanism of Figure 1 is characteristic. More extensive studies were done with asymmetric substitution at the vinyl groups. In these cases regioselectivity favors one of the two possible products. This observation was

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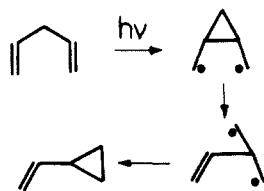
Figure 1. Mechanistic scheme for di-π-methane rearrangement.

supported by CNDO CI calculations[4] on a 1,5-diaryl-1,4-pentadiene moiety. Here the diarylcyclopropyldicarbinyl diradical was studied and it was found that the carbinyl carbons are electron rich in the S_1 state. The calculations led also to the conclusion that weakening of the three-membered ring bond adjacent to the electron donor requires less energy than weakening adjacent to the electron acceptor. It was also argued that the mechanism involving a cyclopropyldicarbinyl diradical is supported indirectly by experimental evidence. The di-π-methane rearrangement does not occur in the absence of the second π bond.[5]

Adam[6] felt that the various diradical species that have been postulated as reaction intermediates require more rigorous confirmation through independent synthesis. He used azoalkanes as precursors for the 1,3-diradical of Figure 1. From his experiments he confirms and extends Zimmerman's scheme. Azo precursors of 1,4-diradicals leading onward to 1,3-diradicals were already mentioned in Zimmerman's work.[1] In work preceding that of Adam, Zimmerman had generated the barrelene related 1,4-diradicals and shown that the triplets did proceed onwards to 1,3-diradicals and thence to semibullvalenes.[7]

The continuing interest in the mechanism of di-π-methane is documented in recently published theoretical and experimental work. Borden et al.[8] calculated geometries and energies of reactant, intermediates, and product for rearrangement on the triplet surface of the parent compound with an STO-3G basis and configuration interaction. They confirm the existence of a cyclopropyldicarbinyl intermediate on the triplet surface. On the other hand experiments by Paquette et al.[9] on triplet sensitized photoisomerization of disubstituted benzonorbornadienes led to the conclusion that cyclopropyldicarbinyl is not involved in the reaction. A similar conclusion is now given by Adam.[10] In this paper we wish to reconcile these seemingly contradictory results.

II. Method of Calculation

We have used the semiempirical molecular orbital (MO) method SINDO1[11,12] to generate the ground- and excited-state potential surfaces. This method was extensively tested for thermal reactions and excited states and in particular applied to photochemical reactions on the configuration interaction (CI) level. The techniques are essentially the same as those used for the explanation of photochemical mechanism of rearrangement and fragmentation of cyclopentanone[13] and diazirines[14] and the ring expansion–ring contraction mechanism of furans.[15]

The ground-state geometries of reactant di-π-methane and product vinylcyclopropane were localized on the SCF potential energy surface by complete geometry optimization with a Newton–Raphson procedure. Bond lengths were optimized to 0.001 Å and angles to 0.1°. The vertical excitation energies were determined by configuration interaction with single excitations from the two highest occupied MOs into the three

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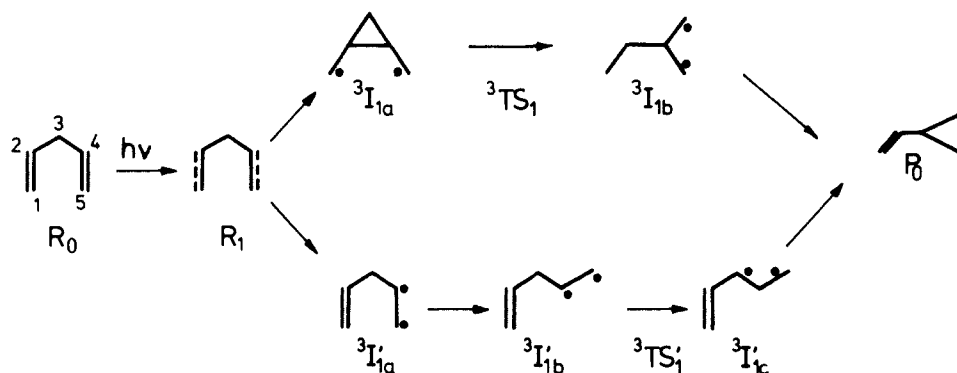(14) Müller-Remmers, P. L.; Jug, K. J. Am. Chem. Soc. 1985, 107, 7275.

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lowest virtual MOs. We labeled the ground states R_0 and P_0, the excited singlet states R_1, R_2, etc., and the triplet states $^3R_1$, $^3R_2$, etc. From the mechanism illustrated in Figure 1 it is apparent that diradicals may be involved as intermediates in the reaction process. We label these intermediates as $^3I_1$ for a minimum on the lowest triplet surface and $^3I_1'$ for another minimum on this surface involving a parallel reaction pathway. If several minima are found on the same surface along one reaction pathway we distinguish these by subscripts a, b, c. The diradicals of Figure 1 will be labeled $^3I_{1a}$ and $^3I_{1b}$ in the following. The transition structure between these two intermediates is called $^3TS_1$.

For the characterization of diradicals we used both Salem's global criterion[16] and our local criterion.[17] According to Salem a diradical is characterized by a singlet–triplet degeneracy. We suggested that a diradical has two atomic centers for which the actual atomic valence numbers are reduced by approximately one for each center. The diradical centers of Figure 1 should have carbon valence numbers close to 3 whereas the normal carbon atoms should have valence numbers close to 4. Details of the method of atomic valence numbers were introduced by Gopinathan and Jug[18] on the SCF level and later extended to the CI level.[19] The valence numbers are calculated as the sum of bond valences between the reference atom and all other atoms in the molecule. The bond valences constitute the covalent sharing of electrons between atoms. They are quadratically dependent on interatomic density matrix elements, whereas the usual bond orders are linearly dependent on density matrix elements. In this sense an atomic valence number represents the actually used covalent bonding capacity of an atom in a molecule calculated from exclusive contributions of all other atoms. For the calculation of diradicals both methods imply the inclusion of at least a double excitation and two single excitations from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO).

After all pertinent intermediates I and transition structures TS were located with an accuracy of 0.005 Å for bond lengths and 0.5° for angles we calculated the corresponding vertical excitations for these structures. This means we compared the resulting MOs at the geometry of $^3I_{1a}$ with the MOs of the reactant R_0 at geometry of $^3I_{1b}$ with the MOs of $^3I_{1a}$, etc., and correlated MOs that were topologically equivalent. This procedure allowed us to correlate the excited states.

III. Results and Discussion

1. Stable and Transition Structures.
The reaction scheme advocated by Zimmerman for the di-π-methane rearrangement is just a partial description of formal pathways leading to vinylcyclopropane. We may characterize it as a ring closure–ring opening mechanism. The first step involves a symmetric 1,4-diradical. Alternatively it is possible to imagine an unsymmetric 1,2-diradical where one of the double bonds is partially broken whereas the other one is retained during the reaction. This mechanism could involve a subsequent rotation about a single bond and hydrogen migration with formation of a 1,3-diradical. Binding between the two centers finally leads to ring closure of the cyclopropane ring. This mechanism is considered and demonstrated in another Zimmerman study.[3] It was shown to occur with an absence of central alkyl substitution. We shall demonstrate that the present theoretical results fit observation. We present these two parallel reaction pathways in Figure 2. Borden et al.[8] have considered the possibility of proceeding on a reaction pathway to $^3I_{1a}$ via $^3I_{1a}'$ but found it rather unlikely. We do not consider this connection here. It seemed appropriate to locate the intermediates I as minima on the lowest triplet surface because the diradicals of Figure 2 can be stabilized only on this surface. In general we expect degeneracy between the ground-state singlet surface and the lowest triplet surface if the energy of the former is sufficiently raised and the energy of the latter sufficiently lowered. Also if a triplet minimum energy is below the singlet ground state energy at the triplet minimum structure, a crossing of singlet and triplet must have occurred for which an approximate region could be estimated. It is therefore clear that a search for a diradical intermediate must be on the lowest triplet surface. These diradical structures were indeed found. It was then only consequential to search for a transition structure $^3TS_1'$ on the lowest triplet surface in order to find a barrier for the hydrogen

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Figure 2. Extended mechanistic scheme for di-π-methane rearrangement.

Table I. Geometries (Å, deg) and Energies (eV) of Ground and Excited States of Di-π-methane

coordinates[a]	structures								
	R_0	$^3I_{1a}$	$^3TS_1$	$^3I_{1b}$	$^3I_{1a}'$	$^3I_{1b}'$	$^3TS_1'$	$^3I_{1c}'$	P_0
12	1.338	1.482	1.402	1.334	1.324	1.332	1.331	1.341	1.339
23	1.534	1.523	1.813	2.551	1.525	1.536	1.500	1.488	1.533
34	1.534	1.523	1.504	1.499	1.529	1.517	1.534	1.491	1.531
45	1.338	1.482	1.478	1.499	1.452	1.457	1.440	1.496	1.504
24		1.539	1.488	1.569					(1.533)
123	129.8	126.1	124.1	111.6	129.9	129.6	129.4	130.1	131.3
234	114.1	60.7			112.2	115.6	122.4	123.0	126.0
345	129.8	126.1	125.3	115.0	125.5	124.4	115.1	113.7	60.6
124		124.0	128.9	129.4					(131.3)
243		59.6	77.5	112.8					(126.0)
245		124.0	126.8	112.8					(126.0)
4321	-106.5				-87.4	-91.2	-91.9	-99.9	-37.3
2345	106.5				88.0	171.4	153.9	177.1	114.5
1243		0	19.0	66.2					(37.3)
1245		-126.1	-104.0	-66.2					(-37.3)
E	0	3.43	3.93	2.90	2.27	2.28	4.86	2.38	-0.28

[a] Atoms labeled as in Figure 2.

Table II. Singlet-Triplet Splitting $\Delta E = E_T - E_S$ (eV) and Atomic Valence Numbers V for Diradical Structures of Di-π-methane

structure	ΔE	atom	V	atom	V
$^3I_{1a}$	0.33	1	3.22	5	3.22
$^3TS_1$	-0.01	1	3.57	5	3.12
		3	3.43		
$^3I_{1b}$	-0.39	3	3.07	5	3.07
$^3I_{1a}'$	-0.42	4	3.13	5	3.10
$^3I_{1b}'$	-0.09	4	3.12	5	3.10
$^3TS_1'$	-0.19	3	3.28	5	3.17
$^3I_{1c}'$	-0.20	3	3.04	5	3.10

migration leading from the 1,2-diradical $^3I_{1b}'$ to the 1,3-diradical $^3I_{1c}'$.

The optimized geometries and energies for these structures are presented in Table I.

The characterization of diradicals in terms of singlet-triplet splitting[16] and valence numbers[17] is given in Table II. All triplet intermediates and the transition structure can be termed diradicals with both criteria.

2. Correlation Diagrams. It was now essential to calculate the vertical excitation energies for intermediates and transition structure for those excitations that correspond topologically to each other. For this purpose we first introduce the following notation. We call the essential atomic orbitals of the two π systems π_{1a}, π_{1b} and π_{2a}, π_{2b}. Localized MOs are called $\pi_1 = \pi_{1a} + \pi_{1b}$, $\pi_2 = \pi_{2a} + \pi_{2b}$ for the bonding MOs and $\pi_1^* = \pi_{1a} - \pi_{1b}$, $\pi_2^* = \pi_{2a} - \pi_{2b}$ for the antibonding MOs. The delocalized MOs are $\pi_+ = \pi_1 + \pi_2$, $\pi_- = \pi_1 - \pi_2$ for bonding combinations and $\pi_+^* = \pi_1^* + \pi_2^*$, $\pi_-^* = \pi_1^* - \pi_2^*$ for antibonding combinations. We present the correlation of the essential orbitals between R_0 and the first intermediates $^3I_{1a}$, $^3I_{1a}'$ in Figure 3. Here we assume that a plane of symmetry is maintained between R_0 and $^3I_{1a}$. The irreducible representations are A' and A''. In both cases the energy of the HOMO is raised and that of the LUMO is lowered so that a diradical can arise.
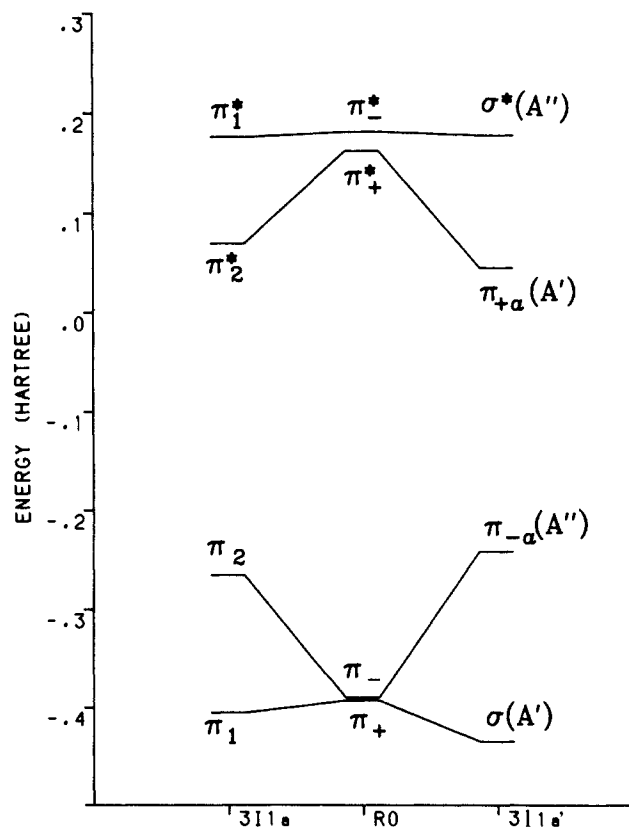
Figure 3. MO correlation diagram for π-orbitals of ground state.

The other two orbitals are almost unchanged from R_0 to $^3I_{1a}'$. On the pathway from R_0 to $^3I_{1a}$ the orbital next to LUMO is almost unchanged, whereas the orbital next to HOMO is sub-
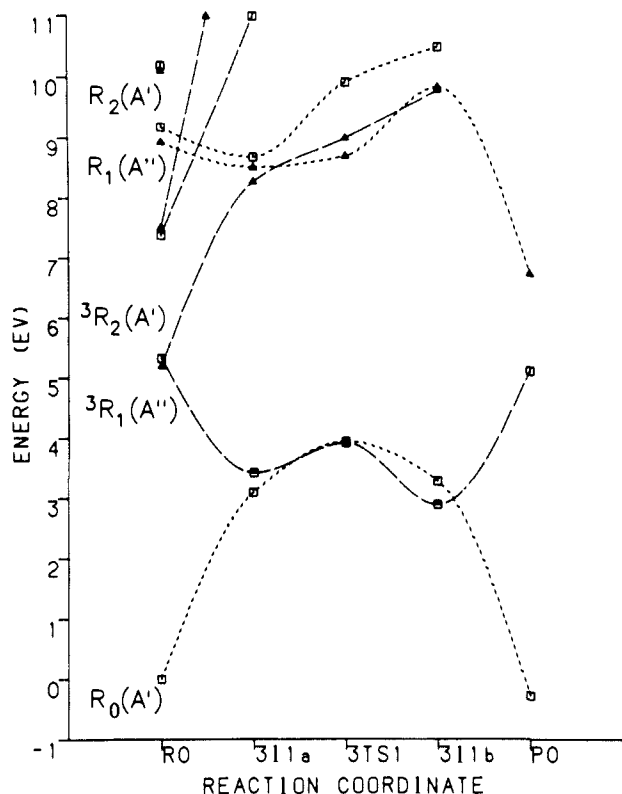
Figure 4. Correlation of states for the ring closure–ring opening mechanism of di-π-methane: singlets (---), triplets (--).

Figure 5. Correlation of states for the hydrogen migration mechanism of di-π-methane: singlet (---), triplets (--).

stantially lowered. This means that excitations from the latter orbital will give rise to high excitation energies for both singlet and triplet states.

In Figure 4 we present a state correlation diagram for ring closure–ring opening. Here it is assumed that a plane of symmetry is maintained in the first step of disrotatory ring closure from R_0 to $^3I_{1a}$. We call this the reactant region. It relates to group C_s with the two irreducible representations A' and A''. The diagram shows the vertical excitations on the left.

The SINDO1 calculations arrive at vertical singlet excitations that are approximately 1 eV too high. This error arises in the valence π–π* excitation of ethylene. Since the error is systematic in π systems of conjugated hydrocarbons calculated with SINDO1, the correlation diagram should be consistent. From the diagram we can exclude a pathway along the first excited singlet surface because of a substantial barrier. However, since singlet $R_1(A'')$ and triplet $^3R_2(A')$ approach each other very closely intersystem crossing should be possible via an unsymmetric vibration of A'' symmetry. $^3R_2(A')$ can relax to the ground-state structure. From there it can relax further via internal conversion to triplet $^3R_1(A'')$. Crossing of this lowest triplet and the lowest singlet at the transition structure $^3TS_1$ between $^3I_{1a}$ and $^3I_{1b}$ can partially lead to the ground state R_0 or proceed further to a second intersystem crossing in the neighborhood of $^3I_{1b}$ from where the product P_0 can be reached.

The barrier of $^3TS_1$ does not provide an obstacle for the process if there is sufficient excess energy. This conclusion was already reached by Dewar in a MINDO/3 calculation[20] on the triplet surface. He found the barrier $^3TS_1$ at 3.80 eV above R_0 compared to our 3.93 eV. His intermediates $^3I_{1a}$ and $^3I_{1b}$ had almost equal energies different from our and ab initio calculations.[8] Since there is a competative rotation as Zimmerman has repeatedly pointed out the product yield would be usually low along this pathway except for cyclic systems. Dewar did not consider the excited singlet state surface that turns out to be essential for enhancement of the rate upon central methyl substitution.

Alternatively the hydrogen migration mechanism is depicted in Figure 5. Here relaxation of R_1 leads to substantial lowering
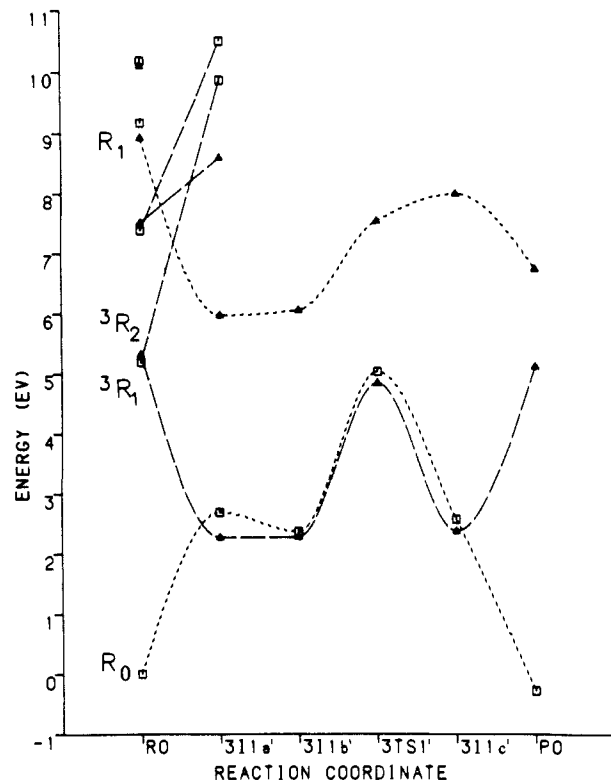
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of the energy. But the system is caught in a potential well on the first excited singlet surface between the structures of $^3I_{1a}'$ and $^3TS_1'$. The barrier is lower than the corresponding barrier in Figure 4. If R_1 relaxes to the triplet surface via intersystem crossing it is caught in a second potential well on the lowest triplet surface $^3R_1$. The barrier for migration makes progress of the reaction toward P_0 less likely than relaxation to the reactant ground state R_0. This may explain the low yield that was found for the phenyl-substituted case.[3]

In the notion of Zimmerman[1] the first pathway is initiated by the simultaneous rotation of the two π groups and the formation of one σ bond. The second pathway corresponds to an initial rotation about one of the π bonds. According to Zimmerman[2] sensitized irradiation involving the triplet leads to cis–trans isomerization because the triplet excitation energy is diverted into a rotation about one of the acyclic π bonds.

In terms of our Figure 4 this would mean that the triplet mechanism is inefficient because intermediate $^3I_{1a}$ is close in structure and energy to the ground state R_0 to which it will primarily relax via an asymmetric stretch and conrotatory ring opening. In this case we expect that the whole mechanism of rearrangement of the unsubstituted di-π-methane is very inefficient in production of vinylcyclopropane.

3. 3,3-Dimethyl-Substituted Reaction. We have repeated the calculation with 3,3-dimethyl-di-π-methane to see which influence substitution has on the two pathways. Although both pathways are qualitatively similar in most features to the pathways of the unsubstituted compound, there is one remarkable difference in the ring closure–ring opening mechanism illustrated in Figure 6. The reaction could proceed in principle on the singlet surface via I_{1a} to I_{1b} from where it could lose its energy either by radiation to the ground state or by intersystem crossing to $^3I_{1b}$ and then to the singlet ground state P_0. The alternative pathway is in Figure 7. Here again barriers on the singlet and triplet surfaces make this pathway of methyl migration less likely. In this case different isomers P_0 and P_0' should result from the two pathways. For P_0 both methyl groups are at the same carbon atom, whereas for P_0' the methyl groups are at different carbon atoms. Since the ring closure–ring opening mechanism is here much more efficient these different products are not found. The present theoretical results
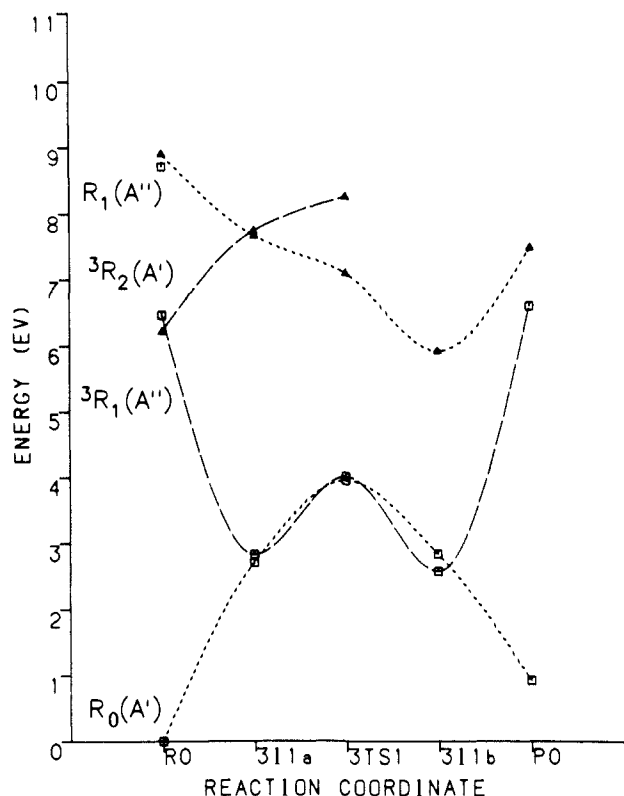
Figure 6. Correlation of states for the ring closure–ring opening mechanism of 3,3-dimethyl-di-π-methane: singlet (- - -), triplets (—).

Figure 7. Correlation of states for the methyl migration mechanism of 3,3-dimethyl-di-π-methane: singlet (- - -), triplets (—).

fit the observation that the second mechanism occurs only in the absence of central methyl substitution.[3]

4. Triplet Efficiency. As Zimmerman demonstrated, triplet efficiency can be quite high in particular cases.[21] In cyclic systems the free rotor effect is not operative and the di-π-methane rearrangement can be studied by triplet sensitization. We wish now to suggest a reconciliation between Paquette's view[9] that the intermediate cyclopropyldicarbinyl $^3I_{1a}$ is not involved in their experiments during the reaction of substituted benzonorbornadienes although they should exist as minima on the lowest triplet potential surface. We see from Figures 4 and 6 that the energy of the $^3I_{1a}$ minimum is higher than the energy of the $^3I_{1b}$ minimum in agreement with Borden.[8] We have also calculated the barrier between $^3I_{1a}$ and $^3I_{1b}$. According to Borden it should be small and not essential for the progress of the reaction. This is in agreement with our finding. However, if triplet sensitization is invoked the triplet $^3R_1(A'')$ is hot, i.e., it has a high vibrational energy because the triplet minimum geometry is substantially displaced from the reactant ground state minimum geometry. If this vibrational energy serves to circumvent the cyclopropyldicarbinyl and reaches the 1,3-diradical $^3I_{1b}$ on a concerted
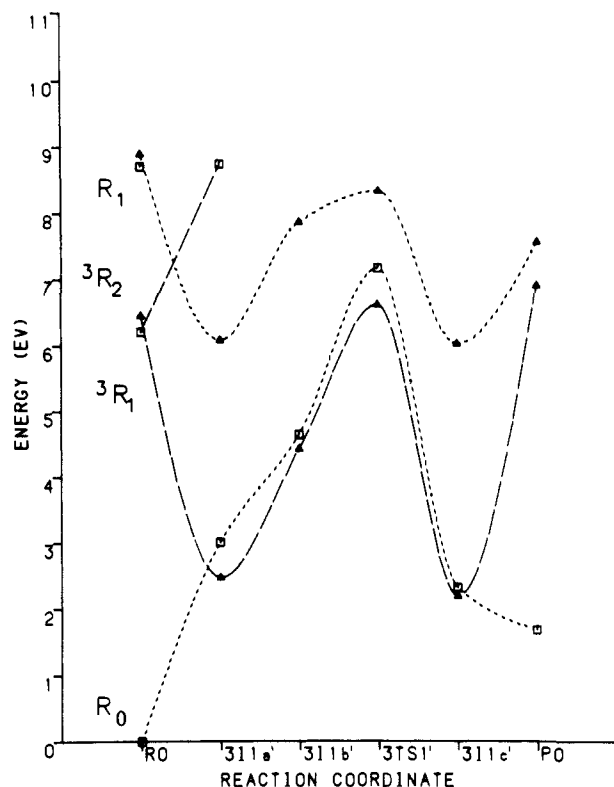
pathway, the product yield should be raised because the back reaction to the ground state via $^3I_{1a}$ is avoided.

IV. Conclusion

We have investigated two mechanistic pathways for the rearrangement of di-π-methane to vinylcyclopropane in the unsubstituted and 3,3-methyl-substituted case. Because of substantial barriers on the lowest excited singlet and triplet surfaces the migration mechanism should be in general less efficient than the ring closure–ring opening mechanism proposed by Zimmerman. For central dimethyl substitution the cyclopropyldicarbinyl is not an intermediate on the singlet surface. One might say that the triplet $^3I_{1a}$ intermediate structure merely serves as a guide toward the essential $^3I_{1b}$ intermediate. In the unsubstituted case the correlation diagrams suggest that the ring opening mechanism is prevented by a high barrier on the singlet surface. So the rate of formation of the parent vinylcyclopropane should be negligible compared to that of the central methyl-substituted system. Here no barrier for ring opening is found. Triplet-sensitized photoisomerization may circumvent the cyclopropyldicarbinyl triplet minimum because of high vibrational energy.

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