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AN MO THEORETICAL STUDY ON THE REACTION OF BENZOCYCLOBUTENE WITH ETHYLENE. CONCERTED VS STEPWISE

TETSUJI KAMETANI, TOSHIO HONDA, YUKIKO EBISAWA and HIROSHI ICHIKAWA*

Hoshi University, Shinagawa, Tokyo 142, Japan

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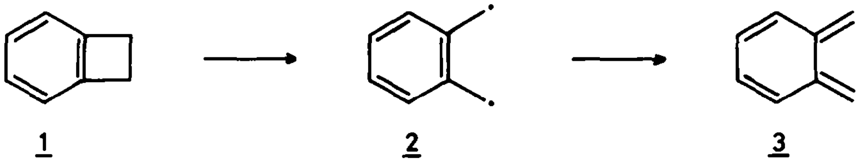
Abstract - In an attempt to determine the reaction mechanism of the Diels-Alder type cycloaddition reaction of benzocyclobutene with dienophiles, the stabilities for the assumed intermediate structures were examined by using MINDO/3, STO-3G, and 4-31G methods. The potential energies of the ring-opening reaction of the benzocyclobutene and cycloaddition reaction of quinodimethane with a dienophile were obtained by MINDO/3 and discussed in relation to the controversial reaction mechanism of the cycloaddition, concerted vs stepwise mechanisms. The results lead to a conclusion that the reaction involves a biradical intermediate followed by a stepwise cycloaddition.

Benzocyclobutene was first synthesized from α,α,α',α'-tetrabromo-o-xylene by treatment with sodium iodide by Finkelstein in 1909.[1] However, any attention had not been paid on its chemistry almost half a century ever since. In 1965, Cava et al.[2] reexamined the same reaction and assumed that o-quinodimethane (3) would be generated as an intermediate in the conversion into benzocyclobutene. The first cycloaddition reaction of benzocyclobutene was published by Jensen in 1962 employing 1,2-diphenylbenzocyclobutene as a diene precursor and maleic anhydride as a dienophile to give the Diels-Alder type adduct.[3] Since this reaction was shown to proceed with high regio- and stereoselectivities in the formation of two carbon-carbon bonds independently by Oppolzer[4] and by Kametani,[5] extensive studies have been carried out on the utilization of benzocyclobutenes as diene precursors to construct naturally occurring compounds.

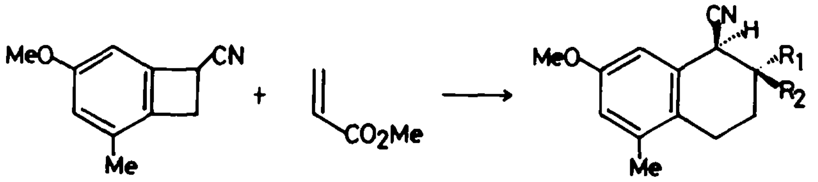


(1)

In spite of its versatile utility, since the intermediate in the reaction has not been isolated, the fundamental problems have remained unsolved on the reaction of 1: namely, whether the reaction passes through the aromatic transition state (the concerted mechanism via

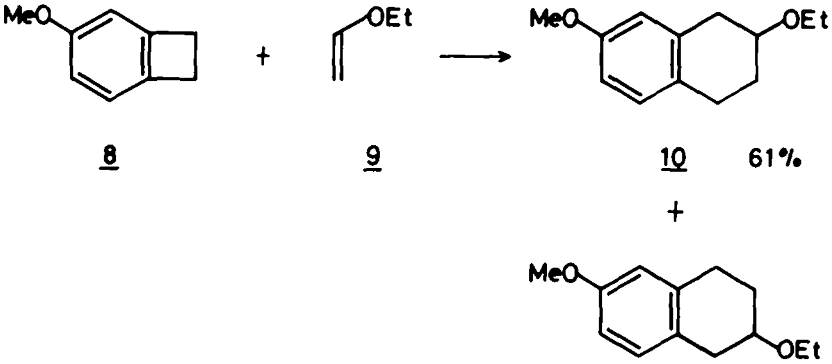
3) or it involves a biradical (the stepwise mechanism via 2). From the organic chemical point of view, both mechanisms seem to be eligible. The intermediate 2 may be stable due to the recovery of aromaticity compensating the energetical unstability of the biradical state while the high reactivity of 3 can be expected due to regaining of aromaticity in the course of cycloaddition reaction.

There have been two divergent mechanisms proposed: Kametani et al.[6] first proposed the biradical theory based on the fact that the reaction of 4 with 5 afforded 6 and 7 where the regioselectivity is held independent of the substituent. This can be reasonably explained by assuming the biradical intermediate. On the other hand, Fleming et al.[7] have observed that the reaction of 8 with 9 gives 10 (61 %) preferentially over 11 (39 %) and reached the conclusion that the reaction is electrocyclic since the preference of 10 can be explained by consideration of the HOMO - LUMO overlapping.



4 5 6: R_1=H, R_2=CO_2Me
7: R_1=CO_2Me, R_2=H

(2)



8 9 10 61%

11 39%

(3)

We consider that the stability of the intermediate plays the most important role in this cycloaddition reaction. Since it may be hard for one to evaluate, by organic chemical intuition, the stability of 2 over 3 and since this reaction seems to be one of topics in synthetic chemistry, we performed an MO theoretical analysis by ab initio STO-3G[8] and 4-31G methods.[9] We also obtained qualitative potential energies (PE's) of the reaction 1 by UMINDO/3,[10] an unrestricted version of MINDO/3,[11] to compare them with those of a typical Diels-Alder reaction (ethylene-butadiene system).

THEORETICAL PROCEDURE

A number of ab initio methods have been provided by quantum chemists. It is well-known that the larger basis set one adopts in the calculation, the better results can be expected. However, at this state of computing facilities, the feasible basis set may be limited to STO-3G or a little better one for the sizable systems as those treated here.

Semiempirical MO methods, MINDO/3 and MNDO,[12] have also been widely used in organic chemistry and the results are generally appreciatable. However, they involve a fundamental difficulty in themselves when applied to intermediate systems: the parameters in MINDO/3 and MNDO theories were so determined that the methods give appropriate heats of formation for the existing molecules.[11,12] Therefore, there is no guarantee that such methods can be used in the intermediate systems. Yet, such calculations have been frequently performed mainly for economical reason. We also used UMINDO/3 for estimation of PE's in the paths of the ring-opening and cycloaddition reactions of 1.

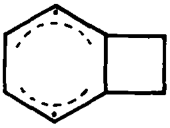
It is often pointed out that the results by MINDO/3 give more appropriate ones than ab initio methods due to inclusion of the correlation effects through parameters. For instance, in some cases of intermediate or non-classical structures, the results by MINDO/3 are shown to be more reliable than the sophisticated ab initio 6-31G* method[13].[14] Apart from preferable computation time, MINDO/3 and UMINDO/3 have the advantages and disadvantages which stem mainly from the fact that the electron correlation is included through parameters. As Dewar stated,[15] use of UMINDO/3 raises two disadvantages. The first is the problem that the unrestricted wave function is not an eigenfunction of the total spin angular momentum operator S^2. This can cause lowering of a few kcal/mol, which we consider negligible if compared with the average errors of MINDO/3. The second problem may be more serious and stems from the MINDO/3 parametrization itself. The unrestricted Hartree-Fock method assigns different spins to different spatial orbials. This introduces a certain amount of electron correlation. Since MINDO/3 is parametrized to include an average correction for electron correlation, the introduction of additional electron correlation leads to energies which are too low, by up to 25 kcal/mol.[15] As will be mentioned, however, the amount of error is ambiguous. Therefore, we did not take any kind of artificial correction for these problems and used in the way that cancels such errors caused by electron correlation.

The geometries of stationary systems were determined by minimizing the total energy with respect to all geometrical parameters, while those in the course of minimum energy reaction path (MERP) were optimized with respect to all parameters except for the reaction coordinate. The reaction has been conducted in an aprotic solvent and it is not considered that there is any participation of solvent to the reacting system. Therefore, we only dealt with the isolated systems.[16]

RESULTS AND DISCUSSION

1. Geometries and Electronic Structures. In an attempt to find out any structural characteristics of the compounds, we compared the calculated structures of 1, 2, and 3 together with those of referential cyclobutene (12) and butadiene (13). Here, it should be noted that the organic-chemical expression 2 shows no more than that 2 is a biradical. Unless electronic excitation is considered, 2 represents the triplet state (T_0) of 3 (defined as 2) or geometrically constrained structure of singlet 3 (defined as 2': one or two of the methylene groups are out of the molecular plane). Table 1 shows the geometrical structures by STO-3G (and 4-31G for 2 and 3) together with previous results.[17,18] (The 4-31G calculation was carried out as the stability of 2 to 3 by STO-3G was reversed by UMINDO/3.)

In the singlet state (S_0), the geometrical and electronic structures of the cyclobutene moiety of 1 do not seem much different from those of cyclobutene. The benzene ring is slightly distorted by fusion of the cyclobutene ring. The triplet state (T_0) of 1 also keeps similarity to that of cyclobutene. However, benzene ring completely loses the outlook of aromaticity. The unpaired electrons in cyclobutene localize on the two carbon atoms which make the double bond in the singlet state. In benzocyclobutene, one unpaired electron delocalizes on a half part of the benzene ring (0.9009, -0.7980, and 0.9778, respectively at C_2, C_5, and C_6) and the other occupies another half part of the benzene with the same values at C_3, C_8, and C_7 (since 1 has the C2v symmetry). There seems to be no bonding interaction of π-electron between them judging from the atomic bond populations and the bond lengths for C_2-C_3 (0.3464; 1.521 A) and C_6-C_7 (0.3518; 1.555 A), which correspond to the atomic bond population and the length for the isolated C-C bond. Therefore, appropriate structural expression of the triplet benzocyclobutene in organic chemistry may be as follows.



Although the geometries around the butadiene moiety of 3 also turned out to be similar to that of the unsubstituted butadiene, the benzene ring is extremely distorted so that it composes of isolated single and double bonds.

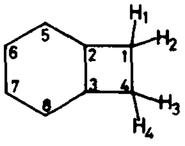
The bond lengths and atomic bond populations in the benzene ring of 2 range from 1.41 to 1.44 A and from 0.44 to 0.47 showing recovery of the aromaticity on the benzene ring.

Table 1. Calculated Geometries of 1, 2, 2', 3, 12, and 13 by STO-3G.[a]

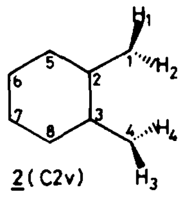
compd.	1	1	2	2	2	2'	3	3	12[b]	12[b]	13[c]	13[c]
elect.st.	singlet	triplet	triplet	triplet	triplet	singlet	singlet	singlet	singlet	triplet	singlet	triplet
symm.	C2v	C2v	Cs(STO-3G)	Cs(4-31G)	C2v	Cs	C2v(STO-3G)	C2v(4-31G)	C2v	C2v	C2v	C2v
C1 - C2	1.5295	1.5302	1.5077	1.4821	1.5071	1.4333	1.3232	1.3309	1.5256	1.5259	1.3137	1.4991
C3 - C4	-	-	1.4205	1.4035	-	1.3441	-	-	-	-	-	1.4046
C2 - C3	1.3895	1.5210	1.4496	1.4315	1.4014	1.4722	1.5091	1.4963	1.3143	1.5506	1.4947	1.4086
C1 - C4	1.5717	1.5727	-	-	-	-	-	-	1.5649	1.5660	-	-
C2 - C5	1.3752	1.3878	1.4141	1.3964	1.3948	1.4032	1.4906	1.4694	-	-	-	-
C3 - C8	-	-	1.4415	1.4274	-	1.4740	-	-	-	-	-	-
C5 - C6	1.3984	1.4162	1.4165	1.3953	1.3840	1.3530	1.3220	1.3284	-	-	-	-
C7 - C8	-	-	1.4055	1.3913	-	1.3399	-	-	-	-	-	-
C6 - C7	1.3867	1.5547	1.4172	1.4016	1.3862	1.4360	1.4767	1.4567	-	-	-	-
<C1C2C3	93.4	90.6	121.1	124.0	121.6	106.8	123.3	123.9	94.7	90.3	126.2	123.9
<C4C3C2	-	-	122.3	122.8	-	125.5	-	-	-	-	-	124.7
<C2C1C4	86.6	89.4	-	-	-	-	-	-	85.3	89.7	-	-
<C5C2C3	122.3	122.7	119.4	119.7	119.1	124.3	116.5	116.7	-	-	-	-
<C8C3C2	-	-	118.1	117.2	-	110.8	-	-	-	-	-	-
<C6C5C2	115.9	116.2	121.4	121.9	121.2	120.8	122.4	122.5	-	-	-	-
<C7C8C3	-	-	121.4	122.0	-	123.4	-	-	-	-	-	-
<C5C6C7	121.8	121.1	119.9	119.4	119.7	118.1	121.1	120.8	-	-	-	-
<C8C7C6	-	-	119.9	119.8	-	122.6	-	-	-	-	-	-
<H1C1C2	115.5	115.0	118.7	119.0	119.0	124.2	121.5	121.0	115.7	114.9	121.5	119.1
<H2C1C2	-	-	-	-	-	-	122.9	123.2	-	-	122.8	-
<H1C1H2	109.2	108.7	116.0	116.4	116.5	111.1	115.6	115.8	-	-	115.7	116.0
H1 - C1	1.0891	1.0895	1.0840	1.0759	1.0846	1.1179	1.0803	1.0724	1.0888	1.0898	1.0812	1.0841
H2 - C1	-	-	-	-	-	-	1.0790	1.0701	-	-	1.0809	-
<H3C4C3	-	-	120.2	120.5	-	121.1	-	-	-	-	-	121.3
<H4C4C3	-	-	122.0	122.3	-	122.8	-	-	-	-	-	121.3
<H3C4H4	-	-	117.8	117.2	-	116.1	-	-	-	-	-	117.4
H3 - C4	-	-	1.0810	1.0711	-	1.0717	-	-	-	-	-	1.0808
H4 - C4	-	-	1.0804	1.0689	-	1.0759	-	-	-	-	-	1.0810
C2 - H5	-	-	-	-	-	-	-	-	1.0818	1.0810	1.0844	1.0855
C3 - H6	-	-	-	-	-	-	-	-	-	-	-	1.0840
<H5C2C3	-	-	-	-	-	-	-	-	134.2	135.6	114.7	118.6
<H6C3C2	-	-	-	-	-	-	-	-	-	-	-	117.4

[a] In terms of A and degree. [b] Ref. 17. [c] Ref. 18.

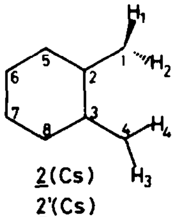
Noticiably, at the most stable geometry (Cs), one of the unpaired electron that belongs to methylene group delocalizes to the benzene ring while the remaining unpaired electron stays isolated. The situation is very similar to that in the triplet state of butadiene: one of methylene groups conjugates with the double bond and one remaining is isolated.



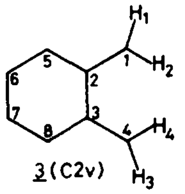
1(C2v)



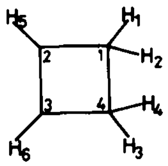
2(C2v)



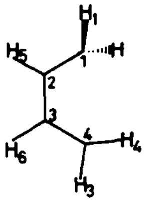
2(Cs)
2'(Cs)



3(C2v)



12(C2v)



13(Cs)

2. Energetic Consideration. An organic chemical consideration estimates that the energy of 2 must be low. It may be a key information for the present problem to know whether it is lower than 3. The total energies of 2, 2', and 3 as well as referential cyclobutene and butadiene are listed in Table 2. The energetic difference between S_0 and T_0 states by both MINDO/3 and ab initio methods agrees in sign except that for 2 and 3. MINDO/3 gives the energy of 2 ca. 12 kcal/mol higher than 3 while STO-3G (or 4-31G) shows that 2 is more stable by 25 (or 4) kcal/mol than 3. The results are dependent on the calculation method and are not in good accordance.

Table 2. Total Energies by MINDO/3[a] and STO-3G[b]

compd.		symm.	MINDO/3	STO-3G
1	singlet	(C2v)	46.9	-303.853321
	triplet	(C2v)	91.6	-303.770102
2	triplet	(Cs)	86.9	-303.823101 (-307.106142)[c]
		(C2v)	-[d]	-303.771847
2'	singlet	(Cs)	128.8	-303.575043
3	singlet	(C2v)	74.5	-303.783849 (-307.100188)[c]
12	singlet	(C2v)	33.0	-153.040343
	triplet	(C2v)	75.3	-152.963697
13	singlet	(C2v)	32.5	-153.017800
	triplet	(C2v)	140.9	-152.956949
		(Cs)	61.7	-152.993440

[a] kcal/mol. [b] a.u. [c] by 4-31G.
[d] Unable to obtain SCF convergence.

Dewar et al.[15] insisted that UMINDO/3 inclines to estimate the energy of open-shell systems too low because of overestimation of electron correlation. If it is always true, the calculated heat of formation, ΔHf, for the triplet state is genarally presumed to be lower. But the differences(ΔE's) by MINDO/3 and UMINDO/3 are not always smaller than these of STO-3G and 4-31G.

We have performed calculation of UMINDO/3 ionization energies of radicals by the intersystem difference (E(R^+) - E(R•), where R^+ and R are alkyl ion and radical) and found that such a calculation satisfactorily reproduces the experimental values and are not always lower than the experimental values.[10c] This means that the overestimation of electron correlation in UMINDO/3 is not always true. We consider that discrepancy of the present case shows a limit of UMINDO/3. Therefore, the results by STO-3G and 4-31G should be emphasized.

Another significant result is that the total energy for 2 of the Cs symmetry is lower than that of the C2v symmetry by 32 kcal/mol by STO-3G. Similar is the referential triplet butadiene. Of organic chemical importance is that one of the unpaired electrons delocalizes and the other purely isolated. That is, the derivatives of 3 have two non-equivalent unpaired electrons, not very reactive one due to delocalization to the benzene ring and the one reactive due to isolation. A regioselectivity has been reported in the synthesis of xylopinine, a protoberberine alkaloid, by application of an intermolecular cycloaddition of the benzocyclobutene derivatives with 3,4-dihydroisoquinolines.[19] We believe that such a regioselectivity is a reflection of the difference of the reactivities.

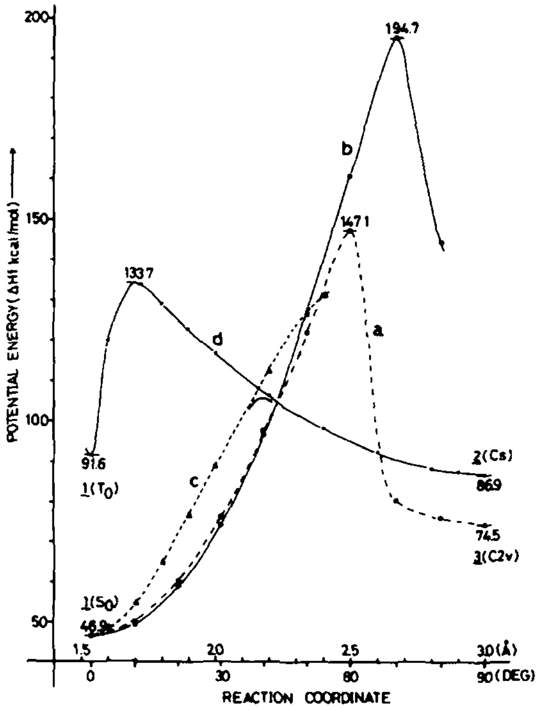


Fig. 1. Relative PE curves for ring-opening reaction of 1 by UMINDO/3.

a: conrotatory, b: disrotatory, c: cleavage without rotation (singlet), d: cleavage without rotation (triplet).

3. Potential Energies in Ring-Opening Reaction of 1. In the previous section, UMINDO/3 was shown to be inappropriate for the present study. However, due to the large size of system, we had to use the method to obtain PE's. The results here, therefore, must be very qualitative. The PE surfaces in terms of ΔHf for ring-opening reaction of 1 by UMINDO/3 are shown in Figure 1. The curves a and b denote the conrotatory and disrotatory reactions while the curves c and d represent the PE curves from 1 to 3 or 2 without rotation in the singlet and triplet states, respectively.

Comparison of the PE's of a and b leads to the conclusion that the conrotatory reaction is favorable agreeing with the prediction by the Woodward-Hoffmann rule.[20] The activation energy by this calculation, however, is as much as 100 kcal/mol. (This value seems considerably high compared with that of cyclobutene (50 kcal/mol) by MNDO.[21]) The reaction of the singlet state without rotation gives a higher PE's than those of rotatory reaction. However, the same reaction in the triplet state gives a lower activation energy and the PE surfaces cross at the distance between two carbon atoms of the methylene groups being around 2.2 A, where the geometries of the two states are not much different. Since the reaction proceeds thermally, the spin conversion from singlet to triplet state is possible. Therefore, the MERP is far lower than the path of the conrotatory reaction. As already discussed, the energy of 2 (equals the triplet state of 3) is low. It is, therefore, easily expected that the triplet state can exist long enough to react with a dienophile. The strong suggestion from the present calculation is that unless the PE's for the following radical reaction are too high, the reaction is regarded as stepwise.

4. Potential Energies for the Reaction of 3 with Ethylene. Determination of PE surfaces may be the most widely accepted method to elucidate the reaction path. As mentioned, however, calculation of transitional energy within Hartree-Fock theory involves various problems especially caused by electron correlation. To reduce such an error, we do not consider the absolute PE's but simply consider the ΔE's (the differences of PE's) of the 3 - ethylene system with those of the typical Diels-Alder reaction: the butadiene - ethylene system.

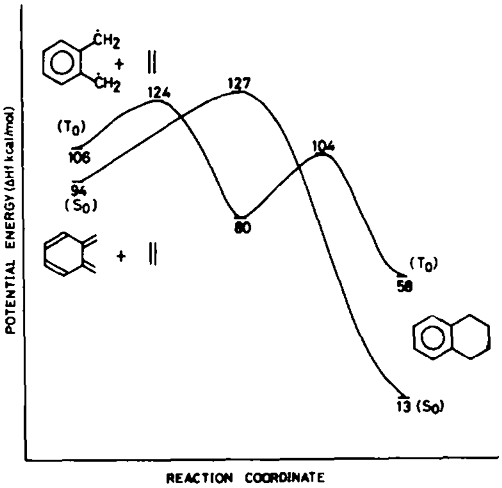


Fig. 2. MERP's for the reaction of 3 with ethylene in singlet and triplet states by UMINDO/3.

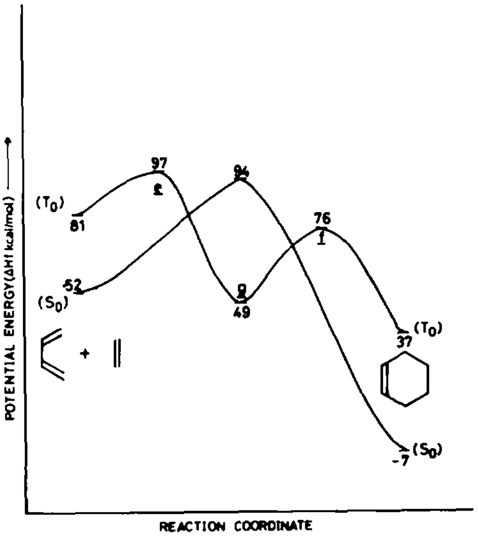


Fig. 3. Referential MERP's for the reaction of butadiene with ethylene in singlet and triplet states by UMINDO/3.

Shown in Figure 2 are the PE curves in terms of heat of formation for the MERP in the singlet state and the triplet state of the 3 - ethylene system whereas Figure 3 shows those of the referential butadiene - ethylene system.

Dewar et al.[15] have performed UMINDO/3 calculation for the conversion reaction of cyclohexene into ethylene and cis butadiene. In the singlet reaction the MERP for the Diels-Alder reaction was found to follow the same PE surface as the reverse reaction. The energy for the transition state of asynchronous reaction is 4 kcal/mol lower than the previous results for synchronous reaction.[15]

The MERP for a reaction should be theoretically same to its reverse reaction. In the triplet states, however, we could not find the same PE's with double transition states as Dewar et al.[15] obtained for the reverse reaction: although we obtained two transition states, e and f, the PE's are, respectively, 20 and 15 kcal/mol higher than the former results. But the energy for g is exactly the same as Dewar's. It should be pointed out that the former results contain an erroneous fact: the heat of formation for the peak corresponding to e has been reported to be 77.1 kcal/mol, which seems strange since the value is lower than the triplet state of the non-interacting ethylene - butadiene system, 81 kcal/mol.

Since the structures of the transition states of the present calculation in the butadiene - ethylene reaction are similar to those of 3 - ethylene reaction, we took our results as the reference reactions. As the Woodward-Hoffmann rule suggests, in 3 or butadiene - ethylene system, the MERP in the singlet state leads to disrotation of two terminal methylene groups. The same reaction in the triplet state involves two potential peaks showing the stepwise reaction. Although the reaction of 2 with ethylene is relatively low compared to the referential reaction, both singlet and triplet reactions are considered eligible. In both systems, the singlet reaction has a unique transition state. But structural difference at the transition state is: the ethylene - butadiene system, as Dewar pointed out,[22] has an asymmetric structure, while in the 3 - ethylene system, the singlet reaction has a symmetric transition state.

5. Concerted vs Stepwise. The calculated MERP's show that as far as the activation energies are concerned, the reaction can occur in either concerted or stepwise way. However, the geometries on potential energy surfaces in the singlet reaction are very different from those in the triplet reaction. This means that intercrossing of PE surfaces with spin conversion is hard to occur. In such a circumstance, the PE surface to follow is determined at the initial state of the reaction. Consequently, energetic stability of the starting system may determine the type of the reaction.

At the initial sate, the energy of the singlet butadiene - ethylene system is far more stable than that of the triplet state. Therefore, the Diels-Alder reaction of butadiene and ethylene is presumed to be a concerted reaction.

According to the STO-3G and 4-31G calculations, 2 is the ground state. If one adopts this result, the following cycloaddition reaction may be a stepwise reaction via the biradical intermediate. Even if the results of ab initio methods are erroneous, at least, 2 may be abnormally stable as a biradical. In addition, the ring-opening reaction of 1 must involve the biradical. Since the stable structure of the biradical has the Cs symmetry, conversion from the triplet state to the singlet state must entail the time for the rotation of the methylene groups. Therefore, the biradical may stay long and may be trapped by the dienophile toward the following cycloaddition reaction. From above consideration, we conclude that the reaction of 1 proceeds via the biradical intermediate resulting in a stepwise reaction.

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