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Mechanism of a Stereospecific, Photosensitized, Cyclization Reaction of 3-Methylene-1,5-heptadiene

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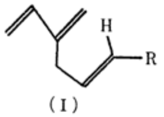
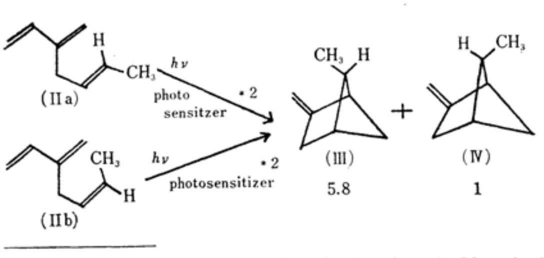
In order to understand the mechanism of the photosensitized, stereospecific cyclization of 3-methylene-1,5-heptadiene, we calculated the electronic state of two intermediates (13 imaginary conformations) by the extended Hückel molecular orbital method and discussed its rotation angle dependency. We obtained the following conclusions. 1) In the two intermediates, the second model (we suppose this to be more like a real intermediate) has lower energy than the first model (we suppose this to be an initial intermediate) both in the ground state and the excited state. 2) If it is necessary for this cyclization that an overlap stabilization exists between two carbon atoms to be bonded and the intermediate has lower energy in that state, the intermediate seems to cyclize after the transition to the ground state singlet. 3) The overlap stabilization between two carbon atoms mentioned above is mainly defined by the interaction between 2p electrons in the highest occupied orbital. This fact coincides with the consequence of the frontier electron theory. 4) The existence of the overlap stabilization between 2p electrons mentioend above corresponds to the fact that the special valence atomic orbital of that two carbon atoms has the same symmetry. This fact is in line with the Woodward-Hoffmann rule on "electrocyclic reactions."

The photosensitized bicyclization reaction of 3-methylene-1,5-hexadiene derivatives (I) has been reported by Charton *et al.*[1], Liu,[2] and Liu *et al.*[3]



(I)

In their reports,[2,3] Liu has shown that either *trans* or *cis* 3-methylene-1,5-heptadiene (IIa or IIb) gave an identical product mixture of two products (III and IV) in a ratio of 5.8 to 1 (in this point this reaction is stereospecific) and regardless of the initial composition of the triene mixture the relative amounts of the two products remained unchanged throughout the reaction and at the same time the relative amounts of the starting materials were found unchanged.



From the fact mentioned above and other facts, he has considered the presence of long lived intermediate (V)*3 in these reactions.

In this report, we calculated the electronic state of an intermediate (V) by Hoffmann's extended

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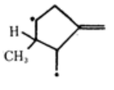
1) J. L. Charlton, P. de Mayo and L. Skattebol, *Tetrahedron Letters,* **1965**, 4679.

2) R. S. H. Liu, *ibid.*, **1966**, 2159.

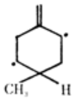
3) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 4936 (1967).

*2 β-Acetonaphthone, triphenylene, benzophenone or fluorenone.

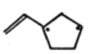
*3 As intermediates, one can also consider the followings.



(VI)



(VII)

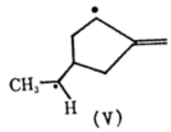


(VIII)

Liu has considered that VI is an unlikely intermediate in these reaction on the grounds of energy considerations.[2] As regards VII and VIII, we found that the following experimental rule exists in these reactions. "In the cyclization of an excited triplet state, intermediates which contain two unpaired electrons in one ring structure, such as VII and VIII, can not exist, while in the cyclization of an excited singlet state the restriction mentioned above does not exist." This rule was justified in the case of the photocyclization of 1,5-hexadiene,[4] 1,6-heptadiene,[5] myrcene,[6] 1,5-cyclooctadiene[7] and neryl acetate.[8]

4) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

5) R. Srinivasan and K. A. Hill, *J. Am. Chem. Soc.*, **87**, 4988 (1965).



(V)

Hückel molecular orbital (MO) method[9] and discussed the mechanism of its stereospecific cyclization.

The Parameters used and the Coordinates

The MO's to describe this system are represented by a linear combination of valence atomic orbitals (AO); that is, the 1s orbital of the hydrogen atom and the 2s, 2px, 2py, 2pz orbitals of the carbon atom. The Coulomb integrals of these AO's, H_{pp}, are given as follows.

$$H_{pp}\ (1s,\ H) = -13.60\ \text{eV}$$

$$H_{pp}\ (2s,\ C) = -21.43\ \text{eV}$$

$$H_{pp}\ (2p,\ C) = -11.42\ \text{eV}$$

The resonance integral between ith and jth AO's, H_{pq}, is calculated by the equation

$$H_{pq} = 0.875(H_{pp} + H_{qq})S_{pq}$$

where S_{pq} is the overlap integral.[9] The effective nuclear charges for these atoms are $Z_H = 1.00$, $Z_C = 3.25$.

The bond distances, the bond angles and the coordinates of models used in this paper are presented in Table 1 and Fig. 1.

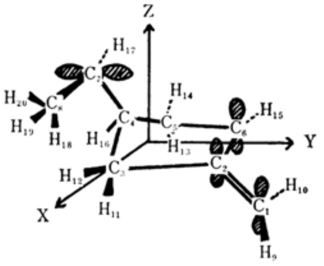
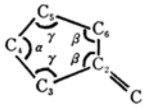
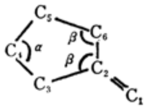


Fig. 1. Coordinates of the model.
(θ: the angle between the C_8, C_7, C_4-plane and the C_7, C_4, H_{16}-plane)

Total energy

$$2\sum_{i}^{\text{occ}} \varepsilon_i = 2\sum_{i}^{\text{occ}}\sum_{p} (C_{pi})^2 H_{pp} + 4\sum_{i}^{\text{occ}}\sum_{\substack{p \\ (p\neq q)}}\sum_{q} C_{pi}C_{qi}H_{pq}$$

TABLE 1. THE BOND DISTANCES AND THE BOND ANGLES USED

C–C distance	
sp^3–sp^3	1.54 Å
sp^3–sp^2	1.52 Å
sp^2–sp^2 (allylic resonanced)	1.40 Å
C–H distance	
sp^3	1.09 Å
sp^2	1.06 Å
bond angle (except otherwise indicated)	
sp^3	109°28′
sp^2	120°
1) first model[*4] (C_1, C_2, C_3, C_4, C_5, C_6 are on the same plane)	
	α: 108° β: 111°03′ γ: 104°57′
2) second model (C_1, C_2, C_3, C_5, C_6 are on the same plane and C_4–C_7 axis is perpendicular to that plane)	
	α: 108° β: 111°03′

Atomic bond population[11] (A.B.P.) in atom pair X–Y

$$4\sum_{p}^{\text{on X}}\sum_{q}^{\text{on Y}}\sum_{i}^{\text{occ}} C_{pi}C_{qi}S_{pq}$$

AO bond population[11] (A.O.B.P.) in AO pair p–q

$$4\sum_{i}^{\text{occ}} C_{pi}C_{qi}S_{pq}$$

Partial AO bond population[11] in AO pair p–q in the highest occupied orbital (HO orbital)

$$4\,C_{p\cdot\text{HO}}C_{q\cdot\text{HO}}S_{pq}$$

Results and Discussion

In cyclopentane, the ring is nearly planar[10] and the intermediate (V) is considered as a long lived one.[2,3] Therefore, it is supposed that the 5-membered ring of the intermediate (V) is planar. The first model refers to this case. Next, if the intermediate (V) cyclizes to III or IV, C_6 and C_7 which are to become bonded in this reaction must approach nearer than in the case of the first model. The second model refers to one of these cases.

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6) a) K. J. Crowly, *Acta. Cient. Venezolana Supl.*, No 1, 194 (1959—1963); *Proc. Chem. Soc.*, **245**, 334 (1962); *Tetrahedron,* **21**, 1001 (1965). b) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964). c) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1892 (1964).

7) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963); *ibid.*, **86**, 3318 (1964).

8) R. C. Cookson, *Pure Appl. Chem.*, **9**, 575 (1964).

9) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1964).

[*4] In cyclopentane, the ring is nearly planar.[10]

10) G. W. Wheland, "Resonance in Organic Chemistry" John Wiley and Sons, Inc., New York (1955), p. 739.

11) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

Figure 2 shows the θ dependence of the total energy in the first model and in the second model. θ is the angle between the C_8, C_7, C_4-plane and the C_7, C_4, H_{16}-plane and is measured from the C_2, C_3, C_5, C_6-plane side of the former plane to the direction of a C_2–C_1 double bond. From Fig. 2, it can be seen that the second model has lower energy than the first model both in the ground state and the excited state. Therefore, it can be supposed that the cyclization of intermediate (V) proceeds *via* the route from the first model to the second model.

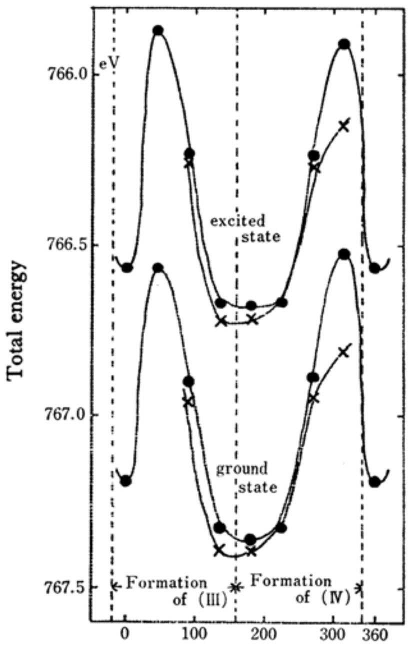

Fig. 2. θ dependence of total energy.
● first model × second model

In the following discussion, we discuss mainly using the first model only for the convenience of calculations and qualitatively one can obtain the same conclusion even if one uses the second model.

Here we suppose that it is necessary for this cyclization that an overlap stabilization[12] exists between C_6 and C_7. Figure 3 shows the θ dependence of the bond energy*5 between C_6 and C_7. In the case of the ground state of the first model, C_6 and C_7 are "bonding" in two θ ranges, the one corresponding to the formation of III, and the other to the formation of IV. If one considers the total energy of these two "bonding" θ ranges, it is apparent that the energy of the fomrer range is lower than that of the latter range. This relation holds also in the second model. In the case of the excited state, C_6 and C_7 are "bonding" in one θ range only, which corresponds to the formation of IV. From the experimental data,[2,3] it is seen that III occurs more than IV. Therefore, the intermediate (V) (excited triplet) seems to cyclize after the transition to the ground state singlet.

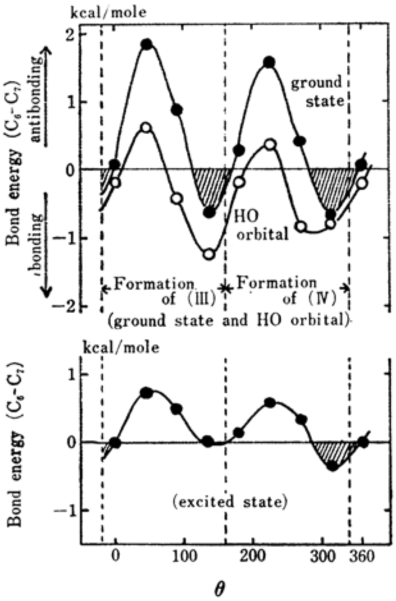

Fig. 3. θ dependence of bond energy (first model).

Furthermore, let us consider the reason why C_6 and C_7 is "bonding" in the special θ ranges only. Figure 3 also shows the bond energy between C_6 and C_7 in the HO orbital. From Fig. 3, it is apparent that the "bonding" in the ground state corresponds to that in the HO orbital. This fact is interesting, because it coincides with the theoretical consequence of the frontier electron theory.[13] From Table 3, it can be seen that the interaction of 2p electrons contributes mainly to this "bonding." Figure 4 shows the atomic bond population and the AO bond population of the ground state and the HO orbital. From Fig. 4, it is apparent that the main reason of the "bonding" is the interaction between $6\,C_{2pz}$ and $7\,C_{2py}$ and this interaction corresponds to that in the HO orbital. Therefore, the phenomenon that C_6 and C_7 is "bonding" is mainly defined by the fact that $6\,C_{2pz}$ and $7\,C_{2py}$ is "bonding."

Next, let us consider the reason why the AO bond population between $6C_{2pz}$ and $7C_{2py}$ in the HO orbital has positive values in the special θ ranges. Figure 5 shows the θ dependence of the coefficients of $6C_{2pz}$ and $7C_{2py}$ in the HO orbital.

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[12] K. Fukui, This Bulletin, **39**, 498 (1966); *Tetrahedron Letters*, **1965**, 2009.

*5 $4\sum_{i}^{occ}\sum_{\substack{p \\ (p\neq q)}}\sum_{q} C_{pi}C_{qi}H_{pq}$

[13] K. Fukui *et al.*, *J. Chem. Phys.*, **20**, 722 (1952); *ibid.*, **22**, 1433 (1954).

TABLE 2. TOTAL ENERGY (eV UNIT) AND ATOMIC BOND POPULATION (first model)

		θ							
		0°	45°	90°	135°	180°	225°	270°	315°
Total energy	Ground state	−767.1967	−766.5647	−766.9025	−767.3217	−767.3632	−767.3259	−766.8888	−766.5244
Total energy	Excited state	−766.5689	−765.8679	−766.2259	−766.6647	−766.6721	−766.6645	−766.2327	−765.9044
A.B.P. (C_6–C_7)	Ground state	−0.000234	−0.003932	−0.001862	0.001290	−0.000556	−0.003304	−0.000864	0.001350

(second model)

		θ							
		0°	45°	90°	135°	180°	225°	270°	315°
Total energy	Ground state			−766.9572	−767.3972	−767.3843		−766.9453	−766.8124
Total energy	Excited state			−766.2594	−766.7183	−766.7130		−766.2694	−766.1502

TABLE 3. BOND ENERGY BETWEEN C_6 AND C_7 (kcal/mol) (first model)

		θ							
		0°	45°	90°	135°	180°	225°	270°	315°
Ground state	2s–2s	0.04	0.03	−0.01	−0.01	0.04	0.04	0.01	0.00
	2s–2p	−0.13	0.14	0.13	−0.11	−0.09	0.11	0.07	−0.16
	2p–2p	0.18	1.69	0.77	−0.51	0.30	1.42	0.34	−0.51
	Total	0.09	1.86	0.89	−0.63	0.25	1.57	0.42	−0.67
HO orbital	2s–2s	0.00	0.00	0.00	−0.00	0.00	0.00	−0.00	−0.00
	2s–2p	−0.20	−0.20	−0.26	−0.28	−0.20	−0.20	−0.24	−0.24
	2p–2p	−0.00	0.82	−0.20	−0.96	0.02	0.56	−0.60	−0.58
	Total	−0.20	0.62	−0.46	−1.22	−0.18	0.36	−0.84	−0.82
Excited state	2s–2s	0.04	0.03	−0.01	−0.01	0.04	0.04	0.01	0.00
	2s–2p	−0.04	0.09	0.06	−0.03	−0.00	0.08	−0.00	−0.11
	2p–2p	−0.04	0.60	0.43	0.03	0.07	0.45	0.33	−0.25
	Total	−0.04	0.72	0.48	−0.01	0.11	0.57	0.34	−0.36

TABLE 4. ATOMIC ORBITAL BOND POPULATION BETWEEN $6C_{2pz}$ AND $7C_{2py}$ (first model)

	θ							
	0°	45°	90°	135°	180°	225°	270°	315°
Ground state	0.000034	−0.001766	−0.000408	0.001226	0.000066	−0.001300	0.000346	0.000778
HO orbital	0.000700	−0.001412	0.000292	0.002364	0.000760	−0.000884	0.001268	0.001532

TABLE 5. COEFFICIENTS OF $6C_{2pz}$ AND $7C_{2py}$ IN THE HO ORBITAL (first model)

	θ							
	0°	45°	90°	135°	180°	225°	270°	315°
$6C_{2pz}$	0.719081	0.719920	0.722513	0.721535	0.720406	0.719852	0.719092	0.711559
$7C_{2py}$	0.030310	−0.061174	0.012585	0.102371	0.032881	−0.038349	0.055131	0.067280

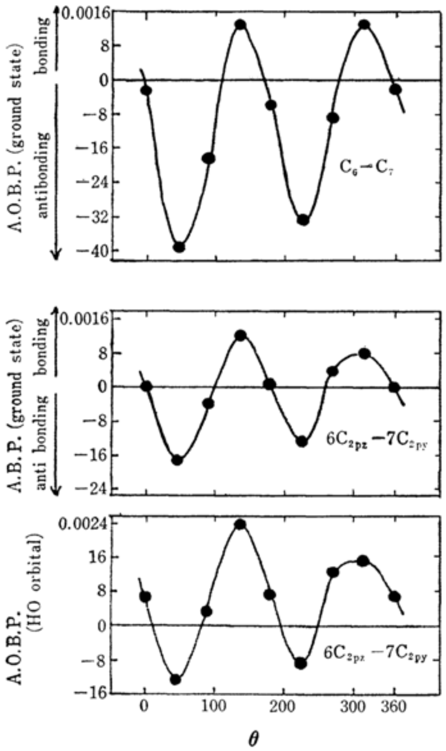

Fig. 4. θ dependence of atomic bond population and atomic orbital bond population.

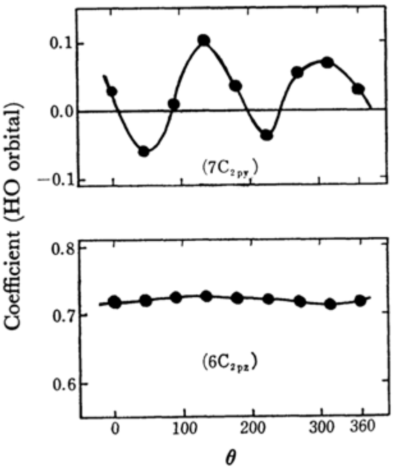

Fig. 5. θ dependence of the coefficients of $6C_{2pz}$ and $7C_{2py}$ in the HO orbital.

From Fig. 5, it is apparent that the phenomenon mentioned above is due to the fact that the coefficients of $6C_{2pz}$ and $7C_{2py}$ have the same sign, in other words, the valence AO of $6C_{2pz}$ and $7C_{2py}$ have the same symmetry in the θ range mentioned above. This fact is interesting, because it is in line with the Woodward-Hoffmann rule on electrocyclic reactions.[14]

The calculations have been carried out on an HITAC 5020 computer at Tokyo University. One of the authors (S.K.) is grateful to Mr. R. Kuroda, Dr. O. Saheki and Dr. T. Irie for their interest in this work. He also wishes to thank the Sumitomo Chemical Industry Co. Ltd. for permission to publish this paper.

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14) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).