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Use of Propagators in the Hückel Model. VII. Thermochemical and Photochemical Rearrangement in Cycloheptatriene, Tropone, and Related Compounds

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Hückel propagator theory has been applied to the analysis of photochemical and thermochemical rearrangement reactions, such as [1,3] sigmatropy, valence isomerization of norcaradiene, Cope rearrangement *et al.* In treatments employing the frontier orbital theory, the molecule is sometimes separated into two parts, and the orbital interaction between specified orbitals of two fragments is taken into account. In the propagator theory, the molecule is always considered as a whole, assuming a resonable transition state. In this transition state, the bond order between sites responsible for the reactions under consideration is estimated, and then the perturbing interaction between these sites is introduced. Then we can evaluate the extra energy to determine whether the reaction occures or not.

In the Hückel model the propagator is expressed in the M.O. basis set $\{|n\rangle\}$ as[1)]

$$G(z) = \sum_{n} \frac{|n\rangle\langle n|}{z-\varepsilon_n}, \tag{1}$$

where ε_n and z are the energy eigenvalue and the complex variable, respectively. Using this propagator, we can easily obtain the bond order q_{rs} between sites r and s, and total energy as[1)]

$$q_{rs} = \frac{1}{2\pi i}\int_c G(r,s;z)\mathrm{d}z, \tag{2}$$

$$E = Tr\frac{1}{2\pi i}\int_c G(z)z\mathrm{d}z, \tag{3}$$

where integration is carried out along the Coulson contour which encloses poles of propagator corresponding to the occupied energy levels, and is assumed to include the spin summation.

In the previous papers, we have presented the perturbation theory[1)] to treat the chemical stability and reactivity,[2)] and the reactivity in the radiation field.[3)] Here we restrict ourselves to take into account the first order term with respect to the perturbation V. This is enough to the following analysis. The first order energy ΔE and that in the radiation field ΔE_f are given as follows:

$$\Delta E = \sum_{r,s} V_{rs}\frac{1}{2\pi i}\int_c G(s,r;z)\mathrm{d}z = \sum_{r,s} V_{rs}q_{sr}, \tag{4}$$

$$\Delta E_f = \frac{n|f_{\mathrm{HL}}|^2}{(\varepsilon_{\mathrm{LH}}-\omega)^2}\sum_{r,s} V_{rs}(q^{\mathrm{L}}_{sr}-q^{\mathrm{H}}_{sr})$$
$$\propto \sum_{r,s} V_{rs}(q^{\mathrm{L}}_{sr}-q^{\mathrm{H}}_{sr}). \tag{5}$$

The former is responsible for the thermochemical reaction, while the latter for the photochemical reaction. In the aboves, q_{rs} and q^{P}_{rs} are, respectively, the bond order and the partial bond order between r and s sites. f_{HL} is the interaction matrix element between electron and radiation field, and n and w are photon number and angular frequency. L and H represent LUMO and HOMO, respectively, and $\varepsilon_{\mathrm{LH}}=\varepsilon_{\mathrm{L}}-\varepsilon_{\mathrm{H}}$. In considering chemical reactivity for possible reaction pathes more over two, we can select, as a preferable reaction path. one with the lowest ΔE or ΔE_f. If the interaction is introduced only between r and s sites, Eqs. 4 and 5 simply become as

$$\Delta E \doteqdot 2Vq_{rs}, \tag{6}$$

$$\Delta E_f \propto Vq^{\mathrm{LH}}_{rs}, \tag{7}$$

where note that $V=V_{rs}=V_{sr}$, $q_{rs}=q_{sr}$, and $q^{\mathrm{LH}}_{rs}=q^{\mathrm{LH}}_{sr}$. The condition that $\Delta E<0$, which indicates the chemical bond being formed, holds for the following two cases:

$$q_{rs} < 0,\ V > 0 \ \text{ or } \ q_{rs} > 0,\ V < 0. \tag{8}$$

The treatment of photochemical reaction is the same as that of thermochemical reaction except that we are using the partial bond order, and the condition that $\Delta E_f<0$ holds for the following two cases:

$$q^{\mathrm{LH}}_{rs} < 0,\ V > 0 \ \text{ or } \ q^{\mathrm{LH}}_{rs} > 0,\ V < 0. \tag{9}$$

Accordingly, we have only to know the bond order or the partial bond order of molecule in question.

The sign of V_{rs} depends on phases of basis sets $|r\rangle$ and $|s\rangle$. Usually the direction of the basis set $\{|r\rangle\}$ is determined so that the resonance integral β should be negative. In the case of π-electron system, and the sign of V_{rs} is negative when $|r\rangle$ and $|s\rangle$ have a facial symmetry, and positive when $|r\rangle$ and $|s\rangle$ have a point symmetry (see Fig. 1(a)).

However, V_{rs} generally has π- and σ-components. The former is perpendicular to the bond axes and the latter parallel. Interaction with the basis set of no direction, for example, the 1s orbital, has only the σ-component (see Fig. 1(b)). These considerations

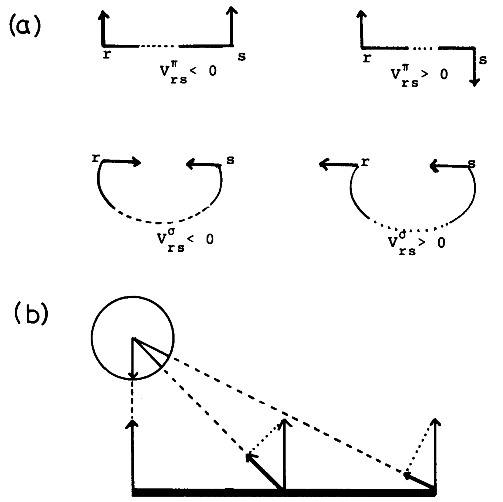


Fig. 1. Example of sign of V_{rs}.
(a) interactions between *p* orbitals, (b) interactions between *s* and *p* orbitals.

play a important role in the sigmatropic and ring closure reactions. For the ring closure reaction, there are two modes named conrotatory and disrotatory. If the π-orbitals are concerned with this, the relationship between the sign of V_{rs} and the mode are as follows ($V^{\sigma}_{rs}=V^{\sigma}_{sr}=V$):

$$V > 0 \text{ ; conrotatory,} \quad V < 0 \text{ ; disrotatory.} \qquad (10)$$

In treating reactivity, the frontier orbital theory and the Woodward-Hoffmann rule are sometimes used. These essence are the orbital interaction between specified orbitals and the conservation of orbital symmetry, respectively. They have made brilliant achievements[4,6] in explaining chemical reactions *e.g.* electrocyclic and sigmatropic reactions. However the former has a tendency of taking into account only for specified orbitals, and in the latter it is difficult to draw the correlation diagram for sigmatropic reaction which does not conserve the orbital symmetry. In the propagator method, the effect of all electrons are counted and we need not take care of the conservation of orbital symmetry at all.

Applications, Comparing with the Frontier Orbital Theory

In this section, We deal with the [1,5] sigmatropy, [1,5] prototropy, [1,3] prototropy, and ring closure reaction of *cis*-butadiene and compare the propagator method with the frontier orbital theory.[4]

Thermochemical [1,3] Sigmatropic Reaction.[6] A few thermal uncatalyzed [1,3] shifts are known. Berson and Nerson made a dramatic observation that the system (a) undergoes a symmetry allowed suprafacial [1,3] shift with inversion at the migrating center, to give (b), at 307 °C.

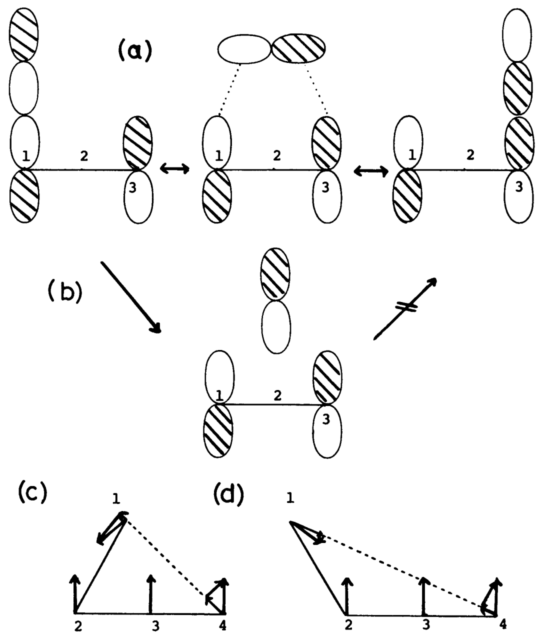
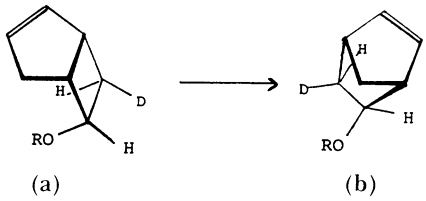


Fig. 2. (a), (b) The reaction path of the [1,3] sigmatropic reaction explained by the frontier orbital theory. (c), (d) The transition state in the [1,3] sigmatropic reaction in our treatment.



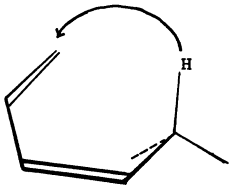
In view of orbital interaction, this reaction is caused by the interaction between SOMO of the allyl radical and the 2pz of carbon. Thus the frontier orbital theory predicts the reaction path shown in Fig. 2(a) rather than Fig. 2(b).

In our treatment of the [1,3] sigmatropy, this reaction is explained as follows: At first, considering the model for the transition state of the sigmatropic reaction as shown in Fig. 2(c), we calculate bond orders and determine signs of π and σ components of V_{rs} as

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 2	0.8944	−	−	−	
1 , 3	0.0000	+	−		
1 , 4	−0.4472	+(−)	0	−(+)	YES(NO)

On the other hand, if we assume the transition state as shown in Fig. 2(d), the calculated results are shown in braces. In this case, it is impossible for the [1,3]-σ tropy to occur. So we conclude that the transition state of the [1,3]-σ tropy is as shown in Fig. 2(c). In the above calculation, for simplicity, all resonance integrals are approximately equal to β and the coulomb integral is put 0.

Thermochemical [1,5]-Prototropy. Now, we deal with the [1,5] prototropy.[4] The treatment is the same as that of the [1,3]-σ tropy.



According to the frontier orbital theory, we consider the interaction between the H-1s orbital and SOMO of pentadienyl radical as shown in Fig. 3(a). In the present method, we assume the transition state as shown in Fig. 3(b) which is also schematically displayed in Fig. 3(c), and proceeds as same as in the case of the [1,3]-σ tropic reaction except for the sign of V_{rs}. In this case, the π-components of V_{1r} are 0 and the σ-component is negative. The result is shown as

Site(r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 2	0.8711	0	−	−	YES
1 , 3	0.0000	0	−		
1 , 4	−0.3877	0	−	+	
1 , 5	0.0000	0	−		
1 , 6	0.3014	0	−	−	YES

When $q_{rs}V_{rs}$ is negative, the shorter R_{rs} is, the more the reaction will occur. Therefore, the hydrogen designated by 1 is most probably transfered to the site 6 ([1,5] sigmatropic reaction). It is noted that the most probable transition state of the [1,5] prototropic reaction is a cis type as shown in Fig. 3(c).

Photochemical [1,3]-Prototropy. The photochemical [1,3] prototropic reaction[6] as

$$CH_3\text{-}CH\text{=}CH_2 \rightleftharpoons CH_2\text{=}CH\text{-}CH_3$$

is easily understood by symmetry characters of orbitals. According to the frontier orbital theory, the reaction is explained by the interaction between LUMO of the allyl radical and the 1s of hydrogen as shown in Fig. 4(a).

While, in our theory this is explained as follows: At first, we assume the transition state shown in Fig. 4(b), and then evaluate the partial bond orders and signs of interaction matrix elements. The results are tabulated in the following:

Site(r , s)	q^{LH}_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 2	−0.4472	0	−	+	
1 , 3	0.0000	0	−		
1 , 4	0.7236	0	−	−	YES

It is quite possible that the photochemical [1,3] prototropic reaction will occur.

Photochemical and Thermochemical Reactions of the Ring Closure of Butadiene. It is well known that in the case of photochemical reaction or thermochemical reaction, the mode of ring closure of butadiene[4] is disrotatory or conrotatory, respectively. According to the frontier orbital theory, the former is explained by the LUMO–LUMO interaction of two

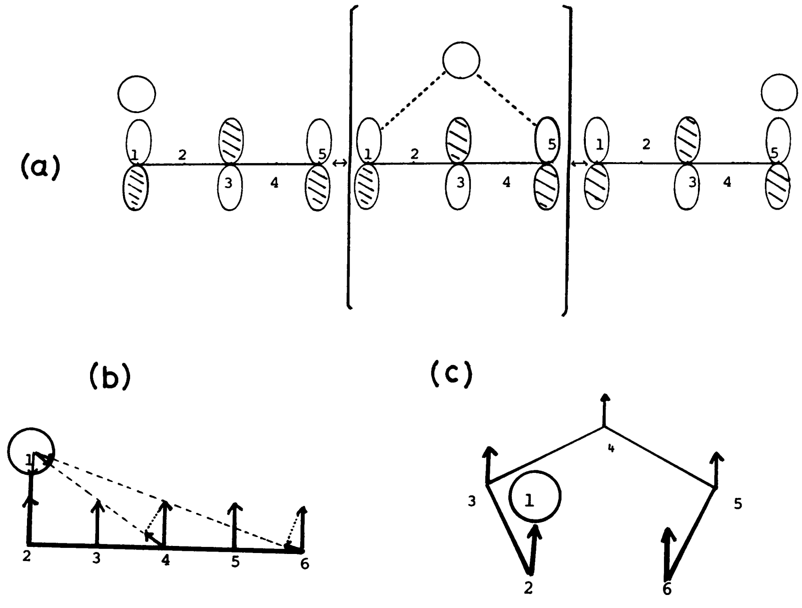


Fig. 3. (a) The reaction path in an example of [1,5] prototropic reaction explained by the frontier orbital theory. (b) The transition state in an example of the [1,5] prototropic reactionin our treatment. (c) The schematic representation of the transition state.

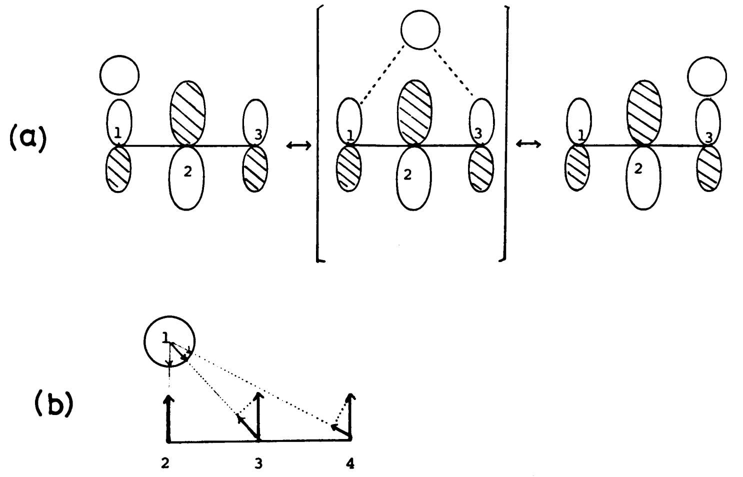


Fig. 4. (a) The reaction path of the photo-[1,3] prototropic reaction explained by the frontier orbital theory. (b) The transition state adopted in our treatment.

ethylene, and the latter by the HOMO–LUMO of two ethylene. (see Fig. 5(a), (b)). This consideration results that the modes of photochemical and thermochemical ring closure are disrotatory and conrotatory mode, respectively.

In view of the propagator method, the treatment is same as previous example, and it is natural to guess the transition state that all the carbons lie on the plane so that V^{π}_{14} and V^{σ}_{14} are negative (see Fig. 5(c)). In the case of photochemical reaction, since $q^{\mathrm{LH}}_{1,4}$ is positive, this reaction occurs with the disrotatory mode. The result is shown as

Site (r , s)	q^{LH}_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 2	−0.4472	−	0		
1 , 3	0.0000	−	0		
1 , 4	0.7236	−	−	−	YES

On the other hand, the thermochemical reaction of this is explained as follows: If the transition state is as same as that of photochemical reaction, this reaction will not occur, because $q_{14}<0$ and $V_{14}<0$. If we consider the transition state where the 2pπ orbitals at sites 1 and 4 twist considerably to the same direction as shown in Fig. 5(d), a positive V^{σ}_{14} shown in brace will produce a slight possibility of the conrotatoty ring closure. However, since V^{π}_{14} is still negative, we can assert this reaction hardly occurs.

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 2	0.8944	−	0	−	
1 , 3	0.0000	−	0		
1 , 4	−0.4472	−	−(+)	+	NO

According to the Woodward-Hoffmann rule, the reactions are explained by the correlation diagrams.⁶⁾

We have compared the propagator method with the frontier orbital theory or the Woodward-Hoffmann rule in these simple thermochemical and photochemical reactions, and get the same results. From now on, we are going to investigate the chemical reaction by the use of the propagator method and, if necessary, compare with the frontier orbital theory or the Woodward-Hoffmann rule.

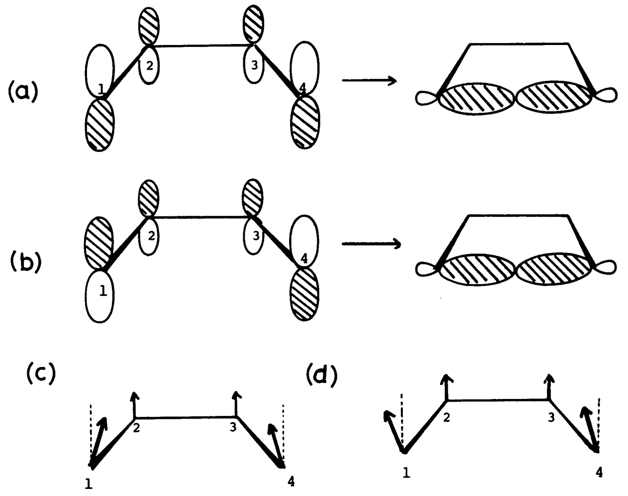
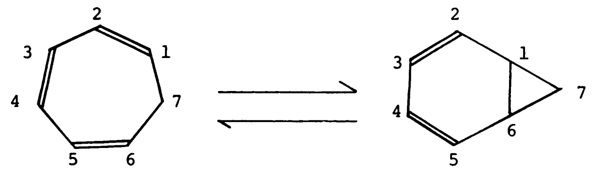


Fig. 5. (a), (b) The ring closure reaction of butadiene in photochemical and thermochemical reactions explained by the frontier orbital theory, respectively. (c), (d) The disrotatory and conrotatory modes of the transition state in the ring closure reacton of butadiene, respectively.

Thermochemical and Photochemical Reactions Cycloheptatriene and Norcaradiene Series

*Cycloheptatriene and Norcaradiene.*⁵⁾ Cycloheptatriene is the valence isomer of norcaradiene and this series undergo many queer rearrangements. We will try to predict these reaction pathes and sometimes compare with treatments with the frontier orbital theory.

It is well known that cycloheptatriene and norcaradiene are with each other in thermal equilibrium.



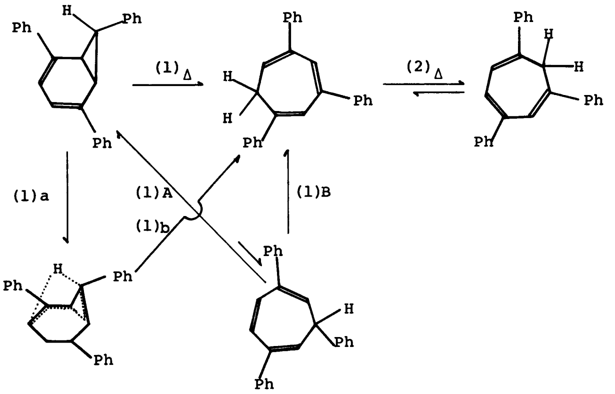
Cycloheptatriene Norcaradiene

It is natural to assume that in the transition state all the carbon atoms numbered from 1 to 7 lie on the molecular plane, but the interactions between sites 1 and 7 and between sites 6 and 7 are neglected because of σ-bond character (see Fig. 6(a)). Thus the treatment is nearly equal that for hexatriene. The result is shown as,

Site (r, s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1, 4	−0.3877	−	0	+	
1, 5	0.0000	−	0	+	
1, 6	0.3014	−	0	−	YES

Therefore it is quite natural that a new bond is formed between sites 1 and 6. By the way, it is mentioned that the ring opening reaction is considerd as the reverse reaction of the ring closure, since all the elementary reactions are supposed to be reversible. According to the frontier orbital theory, this reaction is explained as the interaction of HOMO of heptatriene(see Fig. 6(b)), and the sites 1 and 6 will bind with the conrotatory mode.

*Thermoisomerization of 2,5,7-Triphenylnorcaradiene.*5,8) In this section, we try to predict the mechanism of thermal isomerizations of 2,5,7-triphenylnorcaradiene. First we investigate the step(1)A.



We begin with considering this reaction from the right side to the left side, assuming the transition state as shown in Fig. 7(a) for 2,5,7-triphenylcycloheptatriene. Namely this transition state is the same to that of hexatriene in the ring closure reaction except for three substituting phenyl radicals. The calculated parameters are given as

Site (r, s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1, 4	−0.3681	−	0	+	
1, 6	0.2716	−	−	−	YES
2, 5	−0.0694	−	0	+	

Thus it is probable that between sites 1 and 6 a new σ-bond forms. If it is assumed that the reverse reaction proceeds along the same reaction path, the answer is given.

Next, we deal with the [1,5] prototropy in the step(1)B. It is natural to guess the transition state of 2,5,7-triphenylcycloheptatriene in this reaction is as shown in Fig. 7(b). That is to say, the carbon orbitals at site 7 rehybridizes from three sp^3 orbitals to two sp^2 and a $2p_z$, and then the carbon $2p_z$ binds not only with the H 1s, but also with π-orbitals of the substituting phenyl group and of the cycloheptatriene. Now we assume that for simplicity the resonance integral between H 1s and $2p_z$ at site 7 is nearly equal to β. The result is:

Site (r, s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1, 8	−0.1489	0	−	+	
2, 8	−0.2713	0	−	+	
3, 8	0.1953	0	−	−	YES

Therefore, it is quite possible that H transfers from the carbon site 7 to the carbon site 3 or 4, and our prediction is agree with the experimental result.

In the next reaction(2), only the substituting positions of phenyl groups are different from the previous one. Thus the transition state shown in Fig. 7(c) yields the result:

Site (r, s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1, 8	−0.1488	0	−	+	
2, 8	−0.2799	0	−	+	
3, 8	0.1863	0	−	−	YES
4, 8	0.1786	0	−	−	YES
5, 8	−0.2834	0	−	+	
6, 8	−0.1353	0	−	+	

From these calculations the [1,5] prototropy (in our notation between 3 and 8, or 4 and 8) is quite probable.

According to the frontier orbital theory, the above two reactions are expressed as the orbital interaction between SOMO of cycloheptatrienyl radical and the H 1s (see Fig. 7(d)), but the position of H is not so clear. On the other hand, the position of H is almost fixed in our treatment, because we assume the transition state such that the H 1s binds with the carbon $2p_z$ at site 7.

Then, we try to predict the reaction path (1)a and (1)b. It is natural to assume the transition state as shown in Fig. 7(e). The mutual interaction energy

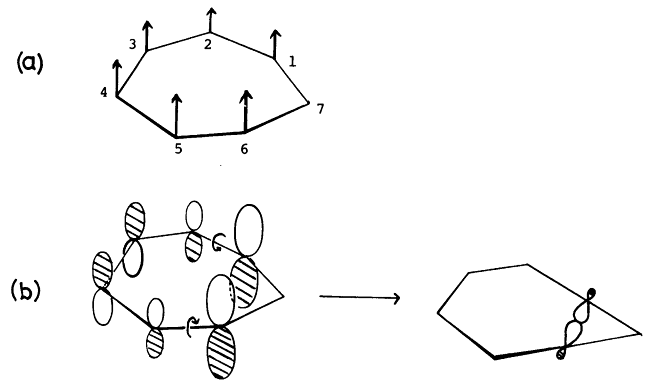


Fig. 6. (a) The transition state of cycloheptatriene in the ring closure reaction. (b) The reaction path from cycloheptatriene to norcaradiene explained by the Woodward-Hoffmann rule.

among three sp^3 hybridized orbitals are approximately, equal to β, because it is nearly equal to be $(\varepsilon_{2s}-\varepsilon_{2p})/4 \fallingdotseq -2\text{eV}$ (ε_{2s}, for example, the orbital energy of the carbon 2s), and the interactions between sites 1 and 7, between 6 and 8, and between 9 and 10 are approximately equal to 2β, because $\beta^{\sigma}_{rs} \fallingdotseq 2\beta^{\pi}_{rs}$. We have the result:

Site (r, s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 10	−0.2326	0	−	+	
2 , 10	−0.0421	0	−	+	
3 , 10	0.0962	0	−	−	YES

Accordingly we may expect that the reaction will occur along this reaction path. But it seems considerably difficult to occur, because $q_{3,10}$ is not so

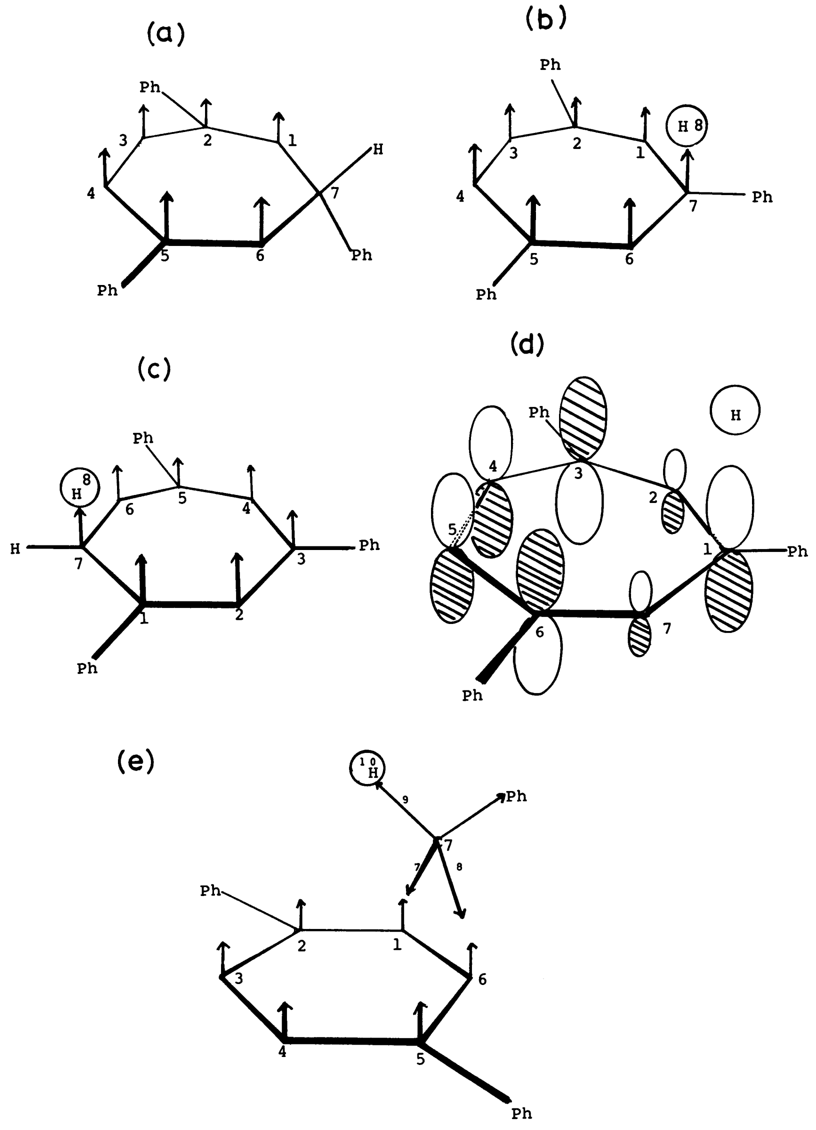


Fig. 7. (a), (b) The transition state of 2,5,7-triphenylcycloheptatriene in the ring closure reaction and the H-transfer, respectively. (c) The transition state of 1,3,5-triphenylcycloheptatriene in the H-transfer. (d) The reaction of 2,5,7-triphenylcycloheptatriene explained by the frontier orbital theory. (e) The transition state of 2,5,7-triphenylnorcaradiene in the H-transfer.

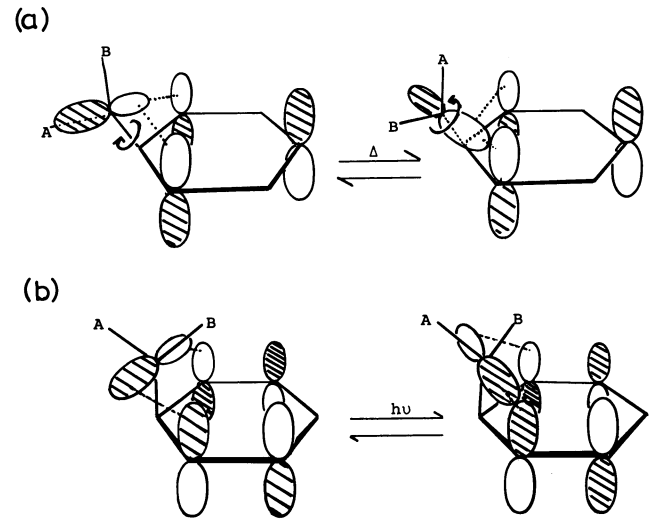
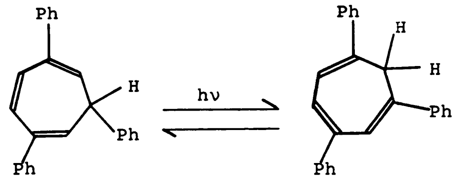


Fig. 8. (a) The reaction path and mode of the Berson-Willcott rearrangement explained by the frontier orbital theory. (b) The reaction path of photochemical isomerization of 2,5,7-triphenylnorcaradiene explained by the frontier orbital theory.

large.

Photoisomerization of 2,5,7-Triphenylcycloheptatriene. In this section we deal with the photochemical reaction of 2,5,7-triphenylcycloheptatriene.[5,9] It is shown as



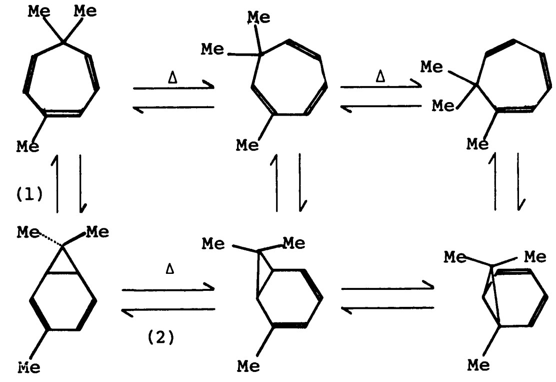
Then assuming the transition state shown in Fig. 7(b), we obtain the result:

Site (r , s)	q_{rs}^{LH}	V_{rs}^{π}	V_{rs}^{σ}	ΔE	reaction
1 , 8	0.2238	0	–	–	YES
2 , 8	0.1399	0	–	–	YES
3 , 8	−0.1745	0	–	+	

Therefore, the hydrogen will transfer from the carbon site 7 to the carbon site 1 or 2, the former being a little more probable. In this case, the former refers [1,7] prototropy and the latter gives the starting material. The same treatment for 1,4-diphenylcycloheptatriene gives the result that perfectly agrees with the experimental one.

BERSON-WILLCOTT Rearrangement

In this section, we deal with the thermoisomerization of methyl-substituted cycloheptatriene,[5] and compare the photoisomerization of triphenylnorcaradiene,[5] because these two reactions are similar in mechanism in spite of their difference in reaction characters.



Berson and Willcott have observed a remarkable serise of the isomerization of methyl-substituted cycloheptatriene[10] as shown above. Woodward and Hoffmann expected that this [1,5] sigmatropic shift had to proceed with retention at the migrating carbon atom[6] as shown in Fig. 8(a). This condition implies that each group substituting the shifting carbon pivots 180° above the cyclohexatriene ring. However we have obtained a different result as will be mentioned below.

The structure of 3,7,7-trimethylcycloheptatriene is the same as that of cycloheptatriene except for the methyl groups at sites 3 and 7. If the carbons designated by 1~6 lying on the molecular plane have $2p_z$ orbitals, the interactions between these are negative, while the effect of two methyl groups at the site 7 are disregarded due to the σ-bond character. Assuming the transition state as shown in Fig. 9(a), we calculate bond orders and determine signs of π- and σ- components of interaction matrix elements:

Site (r , s)	$q_{rs}^{(1)}$	$q_{rs}^{(2)}$	$q_{rs}^{(3)}$	V_{rs}^{π}	V_{rs}^{σ}	ΔE	reaction
1 , 3	0.0661	0.0512	0.0856	–	0	–	
1 , 4	−0.3738	−0.3809	−0.3612	–	0	+	
1 , 5	−0.0231	−0.0168	−0.0307	–	0	+	
1 , 6	0.2913	0.2970	0.2814	–	0	–	YES

Therefore, it is quite possible that the sites 1 and 6 will bind with disrotatory mode (step(1)). This trend is also hold for cases(2; 2,7,7-trimethyl compound) and (3; 1,7,7-trimethyl compound). As is the case of

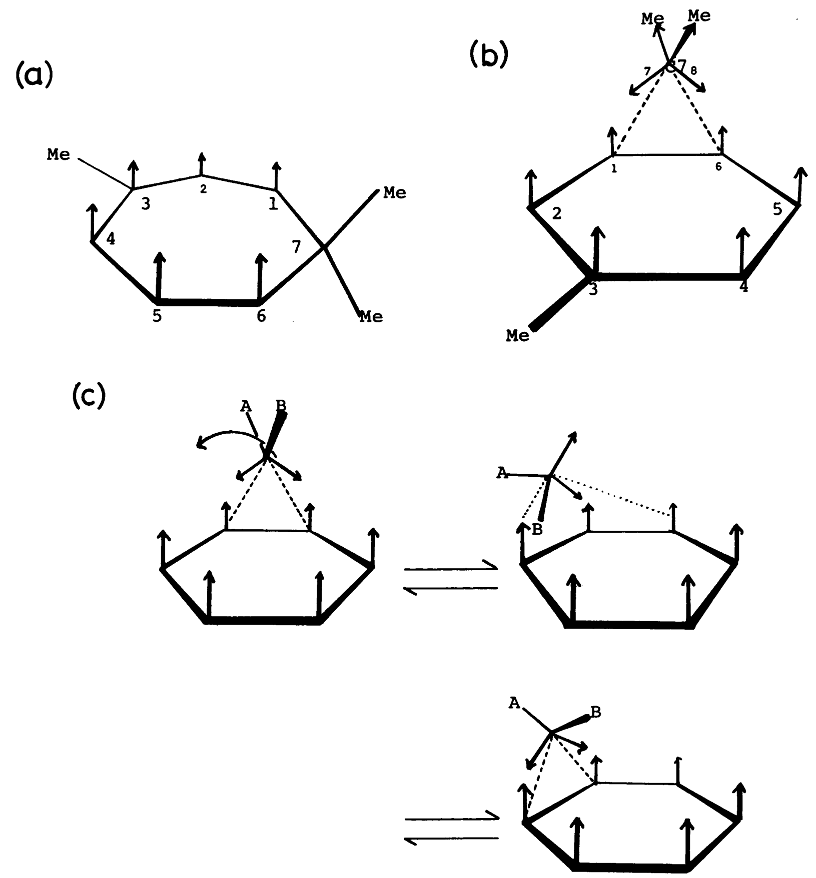


Fig. 9. (a) The transition state of 3,7,7-trimethylcycloheptatriene in the ring closure. (b) The transition state of 3,7,7-trimethylnorcaradiene in the sigmatropic reaction. (c) The reaction path of trimethylnorcaradiene series predicted in our treatment.

cycloheptatriene, we treat the ring opening reaction from norcaradiene to cyclohexatriene as a reverse reaction of the above.

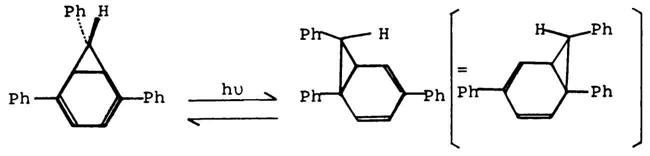
Next we deal with the sigmatropic reaction of step(2). It is natural to guess the transition state shown in Fig. 9(b). Namely, the carbon which would transfer is in the sp^3 character, and the triangle formed by carbons numbered 1,6 and 7 is perpendicular to the molecular plane, and the six carbons lying on the molecular plane are conjugated like in benzene. The effect of two methyl groups is neglected. The interactions are put, $\beta_{17}=\beta_{68}\doteqdot\beta_{78}\doteqdot\beta$, for simplicity. Calculated bond orders and signs of V^{π}_{rs} and V^{σ}_{rs} are shown as

Site (r , s)	$q^{(1)}_{rs}$	$q^{(2)}_{rs}$	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
2 , 7	0.0119	0.0443	+	−		
3 , 7	0.1610	0.1713	+	−	+	
4 , 7	0.0673	−0.0204	+	+	+	
5 , 7	−0.3446	−0.3505	+	+	−	YES
6 , 7	−0.0638	0.0100	+	−		
1 , 8	0.0301	−0.0968	+	−		
2 , 8	−0.3541	−0.3386	+	+	−	YES
3 , 8	−0.0502	−0.0323	+	+		
4 , 8	0.1543	0.1612	+	−	+	
5 , 8	0.0237	0.0190	+	−		

It is quite possible that the sigmatropic reaction will occur without retention at the shifting center shown in Fig. 9(c). Our result is opposite to the prediction by Woodward and Hoffmann. However, the experimental proof has not yet given. The treatment of reactions for the 2-methyl compound is the same as the previous one, and the result is in the above table(2).

According to the frontier orbital theory, the transition state is assumed such that the three menbered ring of norcaradiene is cut at the carbon 7, and the sp^3 orbitals rehybridize to two sp^2 and a $2p_z$. The $2p_z$ and SOMO of cycloheptatrienyl radical interact with each other, so that this reaction occurs with retention at the resting center. Figure 9(c) might help to understand the difference of the reaction mode predicted by the propagator method and the frontier orbital theory.

Next we deal with the photochemical reaction which is similar to the Berson-Willcott rearrangement:9)



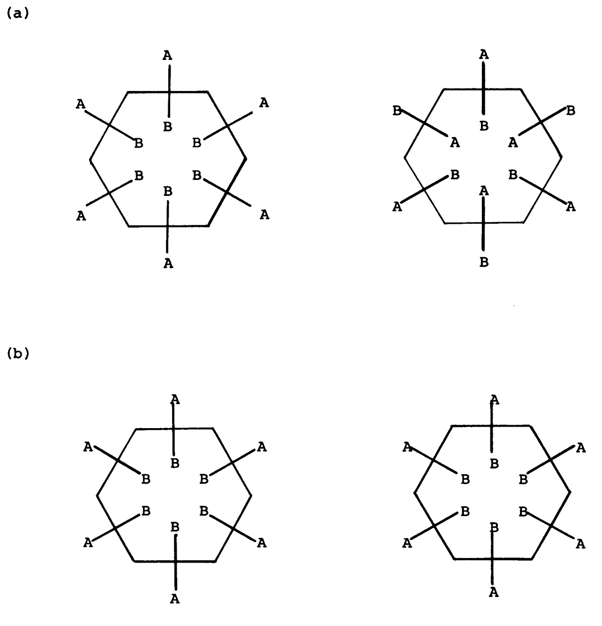
We begin with assuming the transition state of 2,5,7-triphenylnorcaradiene shown in Fig. 7(e) and evaluate the partial bond orders and signs of interaction matrix elements. The result is as follows:

Site (r , s)	q_{rs}^{LH}	V_{rs}^{π}	V_{rs}^{σ}	ΔE	reaction
2 , 7	0.1951	+	+	+	NO
4 , 7	−0.2534	+	−		
6 , 7	0.3373	−	−	−	

Thus we conclude that photoisomerization of 2,5,7-triphenylnorcaradiene which is similar to the Berson-Willcott rearrangement will not occur under the condition that the shifting carbon is in the sp^3-like state. This suggests that the present model of transition state is not adequate. Then we consider a new model that the shifting carbon is in sp^2 and $2p_z$ due to the effect of phenyl group substituting this carbon. It is noticed that there are interaction matrix elements among sp^3 orbitals, but between the sp^2 and $2p_z$ not. Under these considerations, we evaluate partial bond orders and signs of interaction matrix elements. The result is in the following:

Site (r , s)	q_{rs}^{LH}	V_{rs}^{π}	V_{rs}^{σ}	ΔE	reaction
2 , 7	−0.3642	+	+	−	YES
4 , 7	0.2813	+	−		

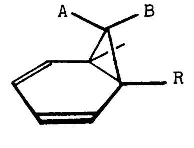
Conclusively, the phenyl group attached to the migrating carbon has a great influence on the photochemical [1,5] sigmatropy, and the shifting carbon may transfer without retention. This result is also explained by the frontier orbital theory, namely, by the interaction between the $2p_z$ of the shifting carbon and LUMO of cyclohexadienyl radical as shown in Fig. 8(b). We show the difference between the reaction mode predicted by the propagator method and that by the frontier orbital theory in Fig. 10.[6]



Propagator method Frontier orbital theory

Fig. 10. The reaction modes of the Berson-Willcott rearrangement and photo-isomerization of 2,5,7-triphenylnorcaradiene predicted by the propagator method and the frontier orbital theory.
(a) Thermochemical reaction, (b) photochemical reaction.

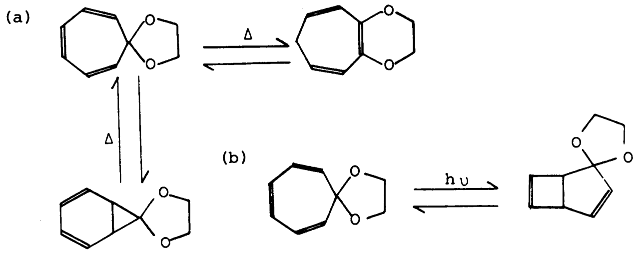
If in the molecule written as



the similar reactions as mentioned in this section proceed with the retention at the migrating center, the slither mechanism is available not to loose the optical activity. However, if we employ the frontier orbital theory, the migrating center pivots in the thermal reaction resulting racemerization. On the other hand, in the optical reaction both treatments give the same results keeping the optical activity.

Photochemical and Thermochemical Rearrangements of Tropone Ethylene Acetal

In this section, we deal with the photochemical and thermochemical rearrangement of tropone ethylene acetal.[5,11]



First we deal with the photoisomerization. It is natural to assume the transition state as shown in Fig. 11(a), where the effect of oxygen can be disregarded because of its σ-bond character. The calculated results are:

Site (r , s)	q_{rs}^{LH}	V_{rs}^{π}	V_{rs}^{σ}	ΔE	reaction
1 , 4	0.4356	−	0	−	YES
1 , 6	−0.5431	−	0	+	
2 , 5	−0.1076	−	0	+	

Therefore, this reaction will occur with disrotatory mode.

Next we consider the thermochemical reaction for two alternative pathes. A and B as shown in the following. We predict which path is suitable.

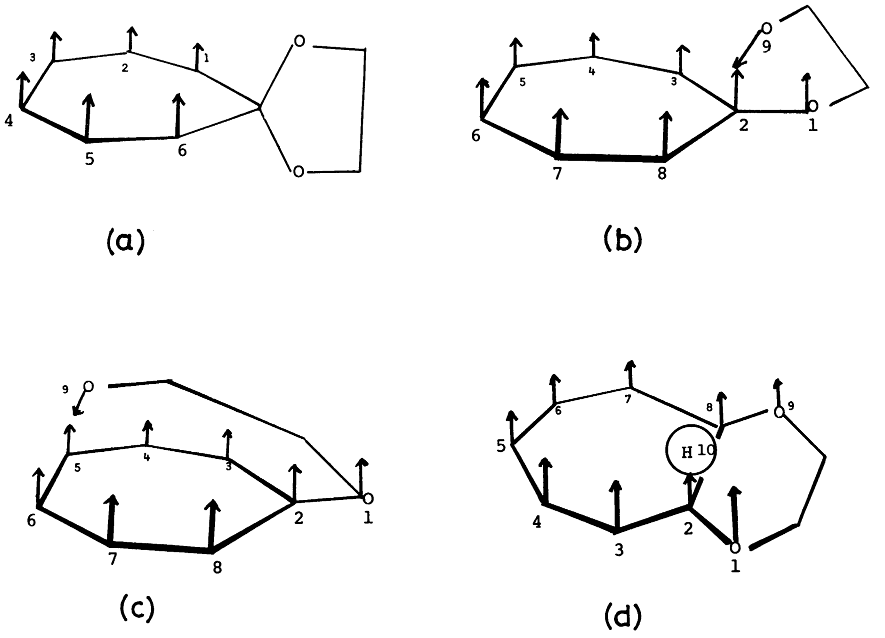
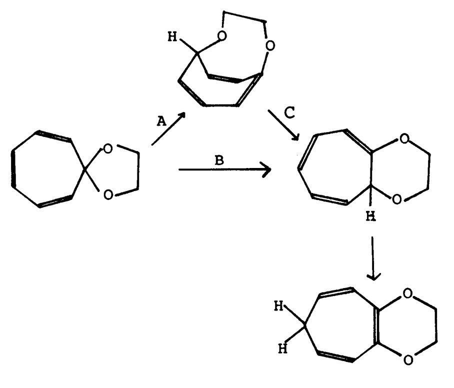


Fig. 11. (a), (b) The transition state of tropone ethylene acetal in the ring closure and O-transfer, respectively. (c), (d) The transition state of intermediate product of tropone ethylene acetal in the O-transfer and H-transfer, respectively.



In the case of the first sigmatropy, we assume the transition state as shown in Fig. 11(b) and obtain the result as

Site (r , s)	q_{rs}	V^{π}_{rs}		V^{σ}_{rs}	ΔE	reaction
1 , 9	−0.1965	+	<	−	+	
2 , 9	0.7639	−		−	−	
3 , 9	−0.1498	+	<	−	+	NO
4 , 9	−0.1952	+	<	−	+	
5 , 9	0.1310	+	<	−	−	YES

Therefore it is quite possible that the [1,5] sigmatropy occurs. This implies the reaction path A to be preferable, and the "NO" for the 3,9 and 8,9 shifts mean the reaction path B is not acceptable. In order to predict the next step reaction, we assume the transition state as shown in Fig. 11(c) to get the results:

Site (r , s)	q_{rs}	V^{π}_{rs}		V^{σ}_{rs}	ΔE	reaction
1 , 9	−0.0438	+		−		
2 , 9	0.1217	−		−	−	YES
3 , 9	−0.2005	+	<	−	+	
4 , 9	−0.1563	+	<	−	+	
5 , 9	0.7960	+	<	−	−	
6 , 9	−0.2004	+	<	−	+	
7 , 9	−0.1976	+	<	−	+	
8 , 9	0.1749	+	<	−	−	YES

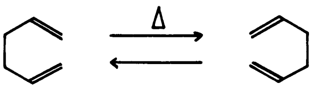
Therefore the reaction will occur on path C. In the above table, the latter "YES" refers to get the product and the former the reverse reaction. What reaction will follow the previous one? We assume the transition state as shown in Fig. 11(d) and calculate as follows:

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 10	−0.1759	0	−	+	
3 , 10	−0.1766	0	−	+	
4 , 10	−0.2808	0	−	+	
5 , 10	0.2220	0	−	−	YES
6 , 10	0.1716	0	−	−	YES
7 , 10	−0.3133	0	−	+	
8 , 10	−0.1020	0	−	+	
9 , 10	0.0052	0	−	+	

It is expected that H will shift from the carbon site 2 to 5 or 6. Here we note that even for complicated reactions mentioned above the propagator method gives nice ways to predict the reaction path correctly.

Cope Rearrangement

Chair, Boat and Quasi-boat Model. The Cope rearrangement[7)] is a kind of the [3,3] sigmatropic reaction as



In view of the frontier orbital theory,[4)] this reaction is explained as the interaction between two SOMO's of allyl radical. Therefore, the transition state of the Cope rearrangement, as is shown in Fig. 12(a)~(c) has three types named chair, boat and quasi-boat type referring to the relative positions of two allyl radicals.

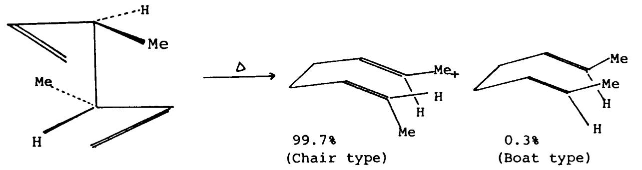
Usually, the Cope rearrangement occurs through the transition state of chair type at low temperature, and the higher the temperature is, the more increasing the product through the boat type is. It is impossible for the simple frontier orbital theory to explain this experimental result, because SOMO of the allyl radical has no amplitude at site 2 so that there is no difference between chair and boat types. Fukui[4)] explained this result by taking account of the interaction between LUMO and HOMO of the allyl radical.

In our treatment of the Cope rearrangement, we begin with assuming the transition state of 1,5-hexadiene as shown in Fig. 12(d) and (e), where at carbon sites 3 and 4 rehybridizations arise from three sp^3 to two sp^2 and a 2p$_z$, so that sites 3 and 4 are coupled through 2p$_z$'s. The resonance integral $\beta_{3,4}$ is approximated to be β for simplicity. Under these conditions calculations are carried out to give

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 4	−0.3877	+	−	?	
1 , 6	0.3014	−	−	−	YES
2 , 5	−0.0867	+ (−)	−	? (+)	(hinderance)

In the above, the results for the boat type are shown in braces. Because of the difference of V_{25}, the transition state of chair type is more stable than that of boat type.

The same treatment explains the following reaction



Thus we understand that the chair type is generally more stable than the boat type.

On the other hand for tropone, the experiment[13)] suggests the quasi-boat rearrangement.

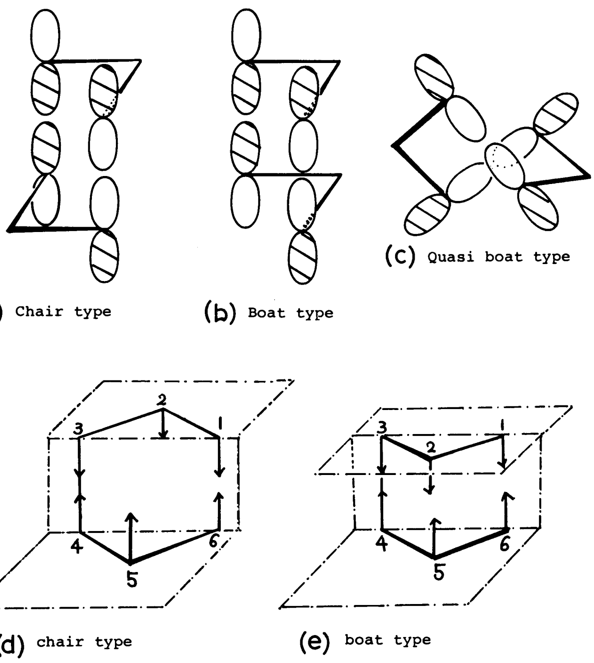
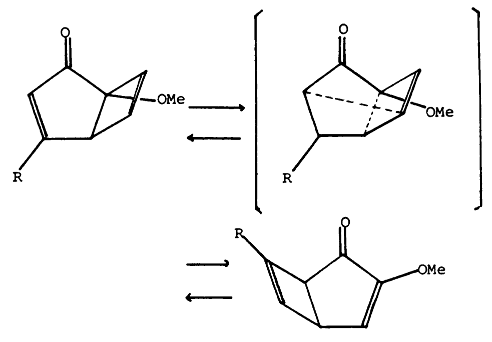


Fig. 12. (a), (b), (c) The possible transition states of the Cope rearrangement in the frontier orbital theory. (d), (e) The transition states of the Cope rearrangement in our treatmemt.



At sight, there be no interaction between two double bonds of molecular ends. If we make a model that carbons at sites 2, 4, 5, 7, and 8 are in sp^2-like state and the carbons at sites 3 and 6 are sp^3-like state, we can find that the σ-bond between sites 3 and 6 has a strain as shown in Fig. 13(a), and the resultant π-components are perpendicular to the left and right planes. So it is natural to imagine two double bond of molecular ends are conjugated with each other through the π-components at sites 3 and 6. As to the coupling parameteres, we put $\beta_{36} \doteqdot 2\beta$, $\beta_{23}=\beta_{34}=\beta_{56}=\beta_{67}=\alpha\beta$ ($\alpha>0$). We have tried two type parameters which are $\alpha=1.0$ and $\alpha=0.5$. The calculated results are shown as (a) and (b), respectively:

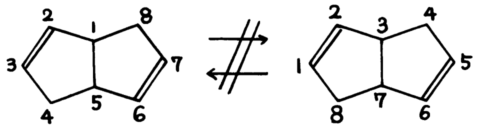
Site (r , s)	$q^{(a)}_{rs}$	$q^{(b)}_{rs}$	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
2 , 4	−0.0580	−0.0080	−	−	+	
2 , 5	−0.1245	−0.0182	−	−	+	
4 , 7	−0.1127	−0.0295	−	−	+	
4 , 8	−0.0285	0.0079	−	−	+ (−)	
5 , 7	0.0496	−0.0026	−	−	− (+)	
5 , 8	0.1273	0.0313	−	−	−	YES

These two treatments give the qualitatively same results. Therefore, it is likely that a bond between sites 5 and 8 may be formed in the transition state in Fig. 13(a) and the reaction path should be such as shown above. Organic chemists[5,7] and R. Hoffmann[6] regard this reaction as a quasi-boat Cope rearrangement, as it is a [3,3] sigmatropic reaction. But this reaction is understood in a little different manner from the Cope rearrangement of 1,5-hexadiene series in the following sense:

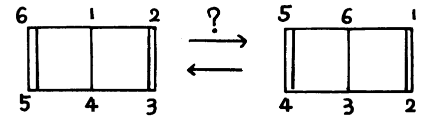
(1) Due to π-components of the 3—6 bond, the double bonds at molecular ends do interact so that the resultant phase of bond order makes the reaction under consideration possible, together with the corresponding interaction matrix elements.

(2) It is also pointed out that in our treatment of the tight-binding approximation, the σ-character of the 3—6 interaction matrix element is fairly large to amount nearly 2β, and this effect is profoundly important in the present result.

Now, we turn to the experimental results. First we concern with the following reaction[14] which actually does not occur.

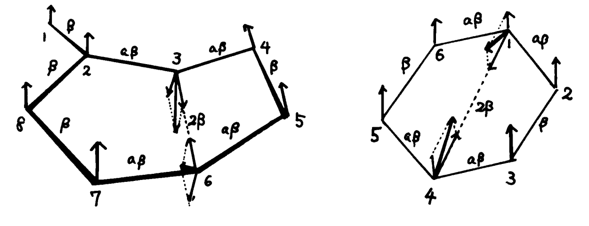


If this reaction would occur, it would be a pure Cope rearrangement through the transition state of the quasi-boat type. In view of our treatment, since the 1—5 σ bond is almost on plane, there is no π conjugation between two double bonds of molecular ends, namely these double bonds are almost independent with each other. Therefore this molecule has no potential to make the rearrangement possible. Also a discussion has been given that, in the Dewar benzene series[15] having similar species of tropone series, the Cope rearrangement will occur through the quasi-boat type. If the reaction would occur, it would be shown schematically as



In view of our treatment, it does not occur. The reason is as follows: First, we assume the transition state of the Dewar benzene series as shown in Fig. 13(b), and calculate as useal. We can find there is no reaction mode in which ΔE is negative.

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
2 , 5	−0.3333	−	0	+	NO
2 , 6	0.0000	−	0		



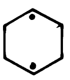
(a) (b)

Fig. 13. (a) The transition state of the Cope rearrangement, through the quasi-boat. (b) The transition state of the Dewer benzene.

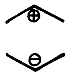
Untill now, we have considered the transition states of the Cope rearrangement: (1) chair type, (2) boat type, (3) quasi-boat type. However in literatures[5,7] we found four type states more than shown as

(4) allyl radical type

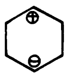
(5) 1,4-biradical type



(6) ion-pair type



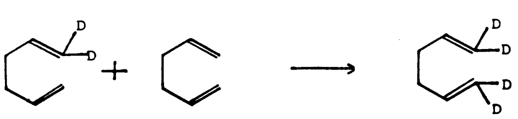
(7) 1,4-dipole type



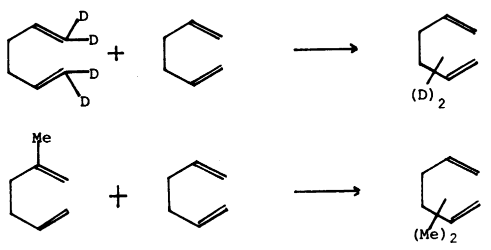
These concepts except (4) can be reinterpretended by our method in the following.

Cope Rearrangement Through the Allyl Radical.

It was said that 1,5-hexadiene was cleaved to two allyl radicals, and each of them had a great concern with the Cope rearrangement at the beginning of reaction, but it was turned out to be uneorrect.[16] Doering[17] reported the next experimental result.

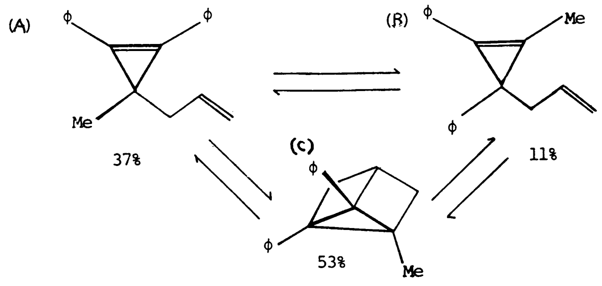


and then Wigfield[18] reported as,



Observing these, it can be asserted that these reactions are of intermolecular character and do not concern with any intramolecular reaction (cleaving into two allyl radicals). We do not discuss these any longer.

Cope Rearrangement Through the 1,4-Biradical. The reaction said to be a Cope rearrangement through the 1,4-biradical[19] is shown as



It is natural for our treatment to guess the transition state of (A) as shown in Fig. 14(a). Then we get calculated parameters as

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 3	−0.0913	+	−		
1 , 6	0.1312	−	−	−	YES
2 , 5	−0.0913	+ (−)	−	(+)	(hinderance)
2 , 6	0.1312	+	−		

In the above, the results for the boat type are in braces. Therefore, we find that the chair type is more stable than the boat type, because $q_{25}V_{25}$ is positive in the latter. In spite of the advantage of the chair type, why does the reaction which seems through the boat type occurs? If we choose the transition state of the intermediate product as shown in Fig. 14(b), the calculated parameters are:

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 5	−0.0460	+	−		
2 , 5	−0.2833	+	0	−	YES
3 , 5	−0.0172	+	−	+	

Therefore, it is possible that this reaction will occur through the boat type.

In addition, we point out the [1,3] sigmatropy could occur, if groups or fragments inside the molecule could prevent sites 1 and 6 from approaching.

The reaction(B) presented at the beginning of this section is treated by the same method, considering effect of the different substituting group. The calculated parameters are:

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 5	−0.0946	+	−		
1 , 6	0.2175	−	−	−	YES
2 , 5	−0.0932	+ (−)	−	(+)	(hinderance)
2 , 6	0.1149	+	−		

In the above, the results for the boat type are shown in braces. Therefore, it is quite possible that this reaction from (B) to (C) will occur through the chair type. Then comparing the value of q_{16} between (A) and (B), we find that this is larger in (B) than in (A), implying that the transition state of (B) is perhaps preferable to that of (A). So the equilibrium probably tends to (A). Our prediction resultantly agrees with the experimental result.

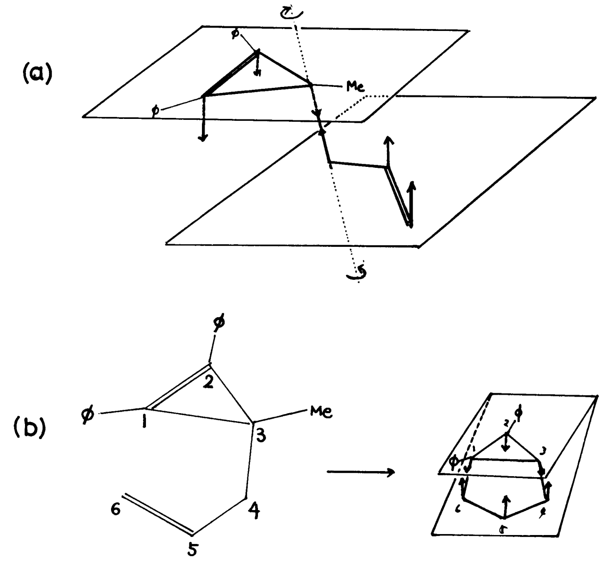
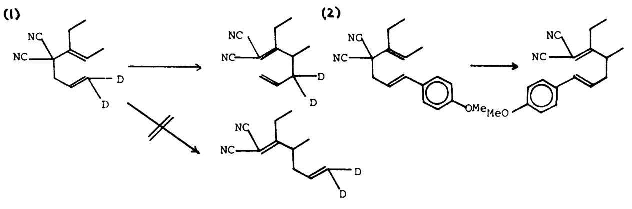


Fig. 14. The transition state of the Cope rearrangement, through the 1,4-biradical.

Cope Rearrangement Through the Ion Pair. The ion pair or dipole models is rather a classical model. It is not acceptable from our viewpoint that the chemical reaction is genereated by quantum mechanical characters of electron, *i.e.* wavefunction or bond order. Employing our method, we can deal with reactions which have been explained by the ion pair model:[20]



The difference between the above two reactions lies in environments, *i.e.*, sites 1 and 6 can easily approach with each other or not. We proceed under the following considerations:

(1) If sites 1 and 6 easily approach, the Cope rearrangenent will occur.

(2) If not, a possibility of the [1,3] sigmatropy increases.

Assuming the transition state for the first reaction as in Fig. 15(a), we calculate necessary parameters as

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 5	−0.0946	+	−		
1 , 6	0.2175	−	−	−	YES
2 , 5	−0.0932	+	−		
2 , 6	0.1149	+	−		

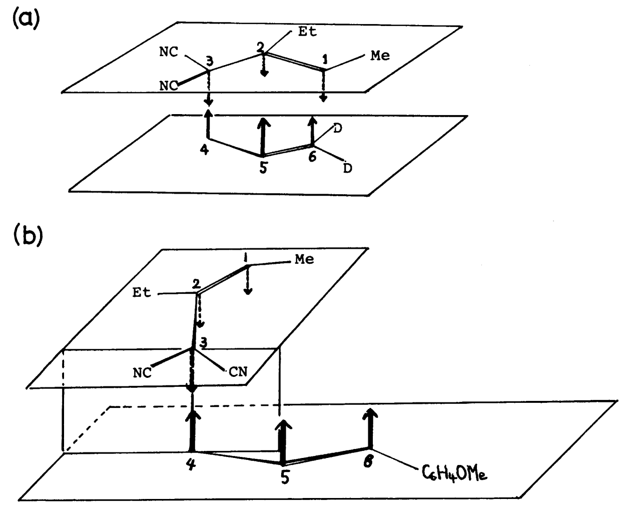


Fig. 15. The transition state of the Cope rearrangement (a) and the [1,3] sigmatropy (b), through the ion pair.

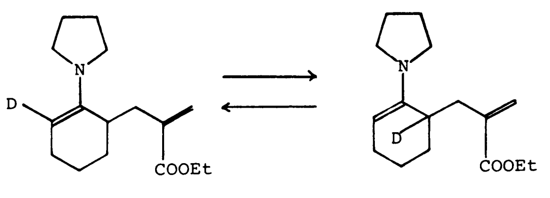
Thus, we can easily explain this reaction as a normal Cope rearrangement through the chair type corresponding to the case (1).

Next, we assume the transition state of the latter reaction as shown in Fig. 15(b), considering steric hinderance similar in the [1,3] sigmatropic reaction. Then we get the results:

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 4	−0.2581	+	$\fallingdotseq 0$	−	YES
1 , 6	0.1897	+	−		
2 , 5	−0.0620	+	−		
3 , 6	−0.2413	+	$\fallingdotseq 0$	−	YES

The possibility of the 1—4 binding ([1,3] sigmatropy) is consistent with the experimental result. While the 3—6 binding is considered to be fairly difficult due to steric hinderance.

Cope Rearrangement Though the 1,4-Dipole Model. We deal with the reaction,



which has been explained to be a Cope rearrangement by the 1,4-dipole model.[21] In this case, either the Cope rearrangement and the [1,3] sigmatropy give the same product. As the steric effects scarcely hinder sites 1 and 6 approaching, we deal with this reaction as a Cope rearrangement. The chair type is sterically less hindered than the boat type is, as shown in Fig. 16. The required calculations are:

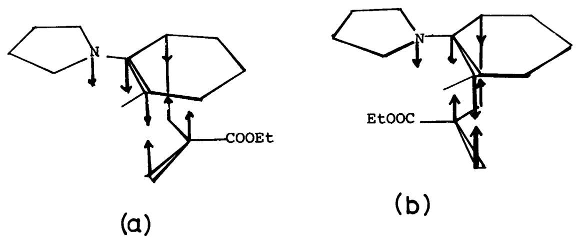


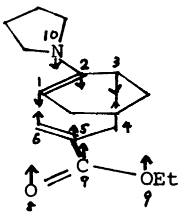
Fig. 16. The transition state of the Cope rearrangement, through the 1,4-dipole. (a) chair type, (b) boat type.

(Chair type)

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 6	0.2070	−	−	−	YES
2 , 5	−0.0705	+	−		

It is noted here that there is little posibility of the [1,3] sigmatropic reaction because of a vanishingly small steric hinderance.

By the way, we examine why the 1,4-dipole model is not adequate. Assuming the structure,



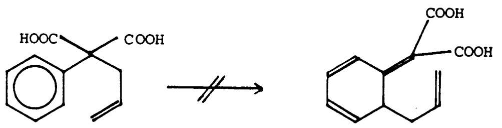
we can easily calculate the π-electron densities in the tight-binding approximation:

Site r	q_r	Site r	q_r
1	1.1347 $\delta-$	2	0.9526 $\delta+$
3	1.0202 $\delta-$	4	0.9823 $\delta+$
5	1.0290 $\delta-$	6	0.8256 $\delta+$
7	0.6489 $\delta+$	8	1.5926 $\delta-$
9	1.8964 $\delta+$	10	1.9172 $\delta+$

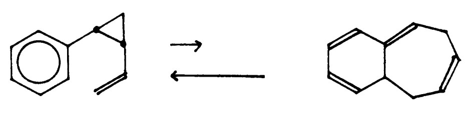
The net charge densitiy at site 7 is qualitatively positive ($\delta+$ in the above table), which is oppositte to the transition state proposed in the reference.[7]

Claisen Rearrangement. The Cope rearrangement in which the double bond of the phenyl radical concerns with rearrangement is called the Claisen rearrangement. We present experimental examples below:[22,23]

(A)



(B)



According to our treatment, we assume a transition state for the reactant of (A) as shown in Fig. 17(a), and evaluate bond orders and signs of interactions as

Site (r , s)	$q^{(a)}_{rs}$	$q^{(b)}_{rs}$	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 4	−0.2901	−0.2351	+	−		
1 , 6	0.1194	0.1706	+	−	−	YES
2 , 5	−0.0512	−0.1020	−	−	+	
3 , 6	−0.1597	−0.2103	+	−		

Then for the product (the right hand), assuming a transition state as in Fig. 17(b), we get bond orders and signs of interactions as in the above table(b).

In the aboves we find a considerbly larger values of q_{16} in the latter than in the former. It suggests the reverse reaction is easier to occur than the forward one does, and then the equilibrium tends strongly to the left. This consideration qualitatively explains the experimental result.

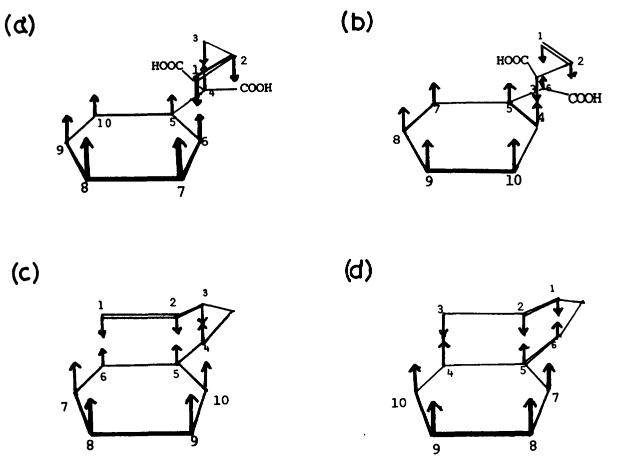


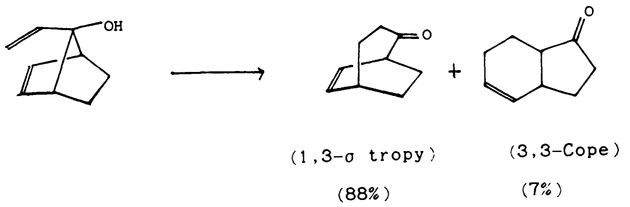
Fig. 17. The transition state of the Claisen rearrangement.

In order to predict the reaction(B), we assume transition states for reactant and product as in Fig. 17(c) and (d), respectively. Evaluated parameters are:

Site (r , s)	$q^{(c)}_{rs}$	$q^{(d)}_{rs}$	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 4	−0.3986	−0.3068	+	−		
1 , 6	0.1628	0.3805	+	−	−	YES
2 , 5	−0.0730	−0.0698	−	−	+	
3 , 6	−0.2195	−0.4503	+	−		

The value of q_{16} being considerably larger in the latter than in the former, the equilibrium seems to lean to the left side. It agrees with the experimental result, too.

Oxy-Cope Rearrangement. This and the related reactions have been classified by Berson[24] as the oxy-Cope rearrangement and the [1,3] sigmatropy systematically. First, we deal with the famous reaction



Remembering the basic considerations previously given about the Cope rearrangement and the [1,3] sigmatropy, we assume the transition state as shown in Fig. 18(a). As to interaction matrix elements, $V^{\sigma}_{16}$is negative, V^{π}_{14}positive and V^{σ}_{14}vanishingly small. Due to the molecular shape, the distance between sites 1 and 6 is rather larger than that between sites 1 and 4. Under these considerations, calculations are carried

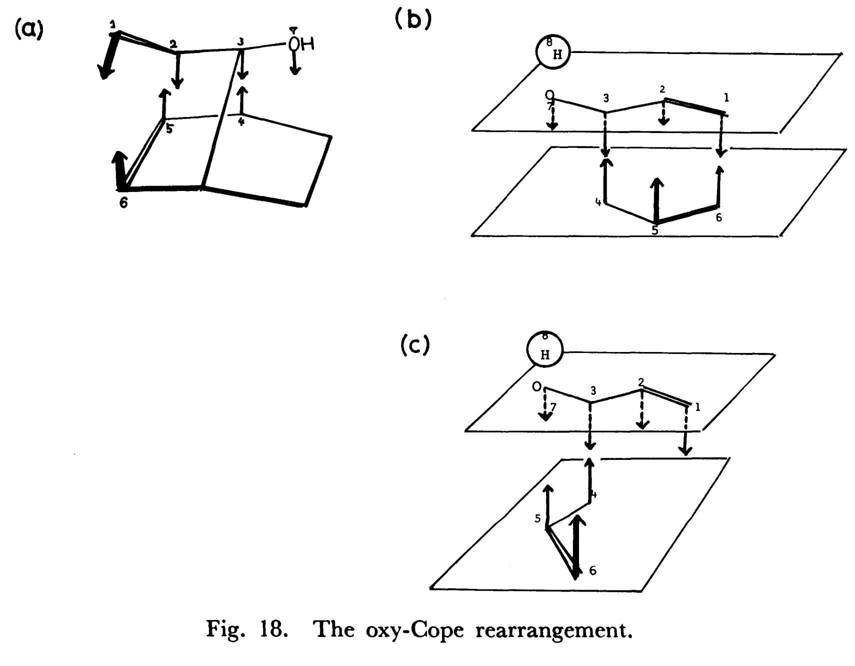
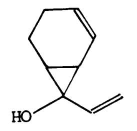


Fig. 18. The oxy-Cope rearrangement.

out as:

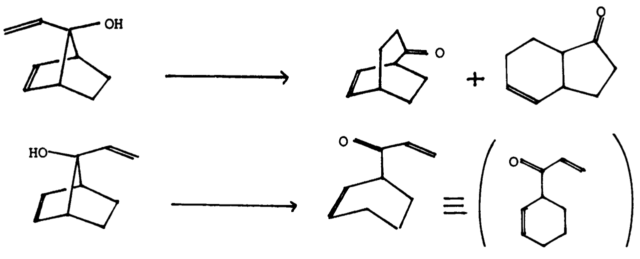
Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 4	−0.3393	+	0	−	YES
1 , 6	0.2012	−	−	−	YES
2 , 5	−0.0748	−	−	+	
3 , 6	−0.3393	≑0	0	−	YES

Therefore, it is quite possible that the [1,3] sigmatropy occurs. In our notation, either the 1,4-transfer and the 1,6-transfer give products shown above, while the 3,6-transfer gives a queer material as



and it will be unstable.

Next, we deal with the competitive reactions, the Cope rearrangement *versus* prototropy shown as



The transition state of this reaction is assumed as shown in Fig. 18(b), and the calculated parameters are:

Site (r , s)	q_{rs}	V^{π}_{rs}	V^{σ}_{rs}	ΔE	reaction
1 , 6	0.2801	−(+)	0(−)	−(?)	YES
1 , 8	−0.2153	0	0		
2 , 8	−0.0674	0	+		
3 , 8	0.2278	0	+	+	
4 , 8	0.1661	0	−	−	YES
5 , 8	0.0169	0	−	+(−)	
6 , 8	−0.1227	0	−		

An other possile transition state is shown in Fig. 18(c). The results derived from this are the values in braces of the above table. These data suggest that only prototropy is possible.

The related reactions are reported by Thies[25)] and by Mukai *et al.*[26)] in other systems.

We expect that the Cope rearrangement will occur when the sites 1 and 6 can easily approach with each other, while the [1,3] sigmatropy takes place when sites 1 and 6 hardly approach due to some steric effect.

Concluding Remarks

From the preceding treatments, we can understand some advantages of our method:

(1) Our treatment is based on a reasonable assumption that the reaction will occur through a transition state in which the perturbing interaction makes energy lowering

(2) Considering the rearrangement reaction by use of the frontier orbital theory, we have to cut some bonds of molecule and take into account the interactions between the specified orbitals(*e.g.* HOMO, SOMO, or LUMO) of fragments. In our method, we need not such unnatural treatments but deal with the system always as a whole, taking into account the effect of all electrons in the molecule. We have only to assume the transition state of molecule in order to evaluate bond orders and interaction matrix elements.

(3) We need not to take care of the conservation of the orbital symmetry which is important in the Woodward-Hoffmann rule. Instead, the mutural phase of bond order at the place where the perturbing interaction takes place plays a important role, together with the sign of the interaction matrix element.

Conclusively we can say our treatment takes a step forward beyond the Woodward-Hoffmann rule or the frontier orbital theory.

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