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An Attempt to Predict Thermal Pericyclic Reactions by a Sequential Nucleophilic Scheme

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A simple, mnemonic method for predicting pericyclic reactions in ground states has been worked out by treating a multi-center reaction as a sequence of one-center reactions analogous to nucleophilic substitution type reaction. The analysis of reaction is carried out by illustrating localized MO's and their stepwise transformation. This method can lead to predictions for thermal pericyclic reactions in agreement with the Woodward-Hoffmann rules and the HOMO-LUMO interaction method. A simple modification of this method is applicable to reactions in excited states.

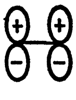
The usefulness and cogency of the principle of conservation of orbital symmetry by Woodward and Hoffmann[1] and the HOMO-LUMO interaction method by Fukui[2] in rationalizing cyclic concerted reactions are now indisputable. The Hückel-Möbius/4N+2—4N method by Zimmerman[3] and Dewar[4] is a theoretical interpretative alternative for the reactions as well as the MO-following method by Zimmerman.[5] In these methods, each MO interaction at reaction centers is naturally treated in a one-step manner.[6] The orbital phase continuity principle approach by Goddard III based on GI wave functions can also lead to the same predictions for thermal reactions,[7] in which the orbital phase changes are treated stepwise.

In the field of classical organic chemistry, an attempt to explain the stereochemistry of E2 reaction, one of two-center non-cyclic concerted reactions,[8] by analogy with that of S_N2 reaction, a one-center concerted reaction, has appeared[9] but without attracting much attention; this type of analogy can be found in not a few reactions.

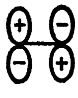
We have attempted to find an alternative method to estimate the allowability or prohibition of the reaction. The present paper is concerned with this new approach, which involves the following treatments: (1) a multi-center reaction is dealt with as a sequence of one-center reactions, and similarly, addition and elimination processes are treated as a combination of substitution processes respectively; (2) these one-center reactions should proceed *via* the process analogous to S_N2 type reaction;[10] (3) the nucleophilic processes are treated qualitatively using localized MO's; (4) the allowability of the reaction is predicted by considering the bonding character of the orbital finally generated after the sequence of nucleophilic processes.

Results

The bonding and antibonding MO of the ethylenic π system are drawn as follows:

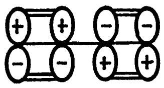


$\phi=\chi_1+\chi_2$
Bonding MO



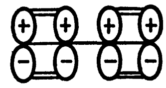
$\phi^*=\chi_1-\chi_2$
Antibonding MO

In ground states, an electron-pair occupies the bonding MO which lies on the lower energy level. According to the localized MO concept, the π-system of butadiene consists of two independent ethylenic π-systems. Thus, the π-bonding MO's of butadiene can be represented as follows:



$\chi_1 \quad \chi_2 \quad \chi_3 \quad \chi_4$

and



$\chi_1+\chi_2=\phi_1$
$\chi_3+\chi_4=\phi_2$

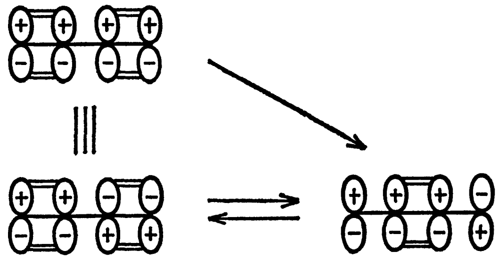
Since these two ethylenic π-systems are regarded to be independent of each other, the phase of AO's between the two systems can be taken arbitrarily. Consequently, each MO representation for butadiene is adoptable.

Let us consider the following reaction process:

$$\underset{\mathrm{I}}{CH_2\text{=}CH\text{-}CH\text{=}CH_2} \rightleftharpoons \underset{\mathrm{II}}{\overset{+}{C}H_2\text{-}CH\text{=}CH\text{-}\overset{-}{C}H_2} \qquad (1)$$

$$\begin{array}{lll} \phi_1 \quad \phi_2 & & \phi_1' \quad \chi_4 \\ \phi_1^* \quad \phi_2^* & \chi_1 & \phi_1'^* \\ \phi_1=\chi_1+\chi_2 & \phi_2=\chi_3+\chi_4 & \phi_1'=\chi_2+\chi_3 \\ \phi_1^*=\chi_1-\chi_2 & \phi_2^*=\chi_3-\chi_4 & \phi_1'^*=\chi_2-\chi_3 \end{array}$$

If the reaction I→II proceeds concertedly, it can be initiated through the interaction between ϕ_1 and ϕ_2^*;[11] the reaction system gains the delocalization energy by this interaction, and the reaction is promoted.[12] In order that the bonding interaction arises between ϕ_1 and ϕ_2^*, χ_2 and χ_3 should face the phase in the same direction, and χ_3 and χ_4 in the inverse direction in the transition state. If the process I→II is concerted, the reverse reaction,



$\mathrm{I_O}$ $\qquad$ $\mathrm{II_O}$

Scheme 1.

II→I, should proceed also concertedly through the bonding interaction between χ_4 and $\phi_1'^*$: in which χ_4 and χ_3 face the phase in the same direction, and χ_3 and χ_2 in the inverse direction. Orbital χ_1 which becomes vacant in II is always in the same, invariable phase. When the process I→II→I is concerted, it can be represented by the following scheme (Scheme 1).[13,14)]

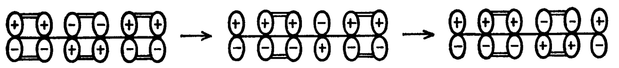
In the following concerted reaction of hexatriene which is considered to comprise a butadienic and an additional ethylenic system,

$$\underset{\text{III}}{CH_2=CH\text{-}CH=CH\text{-}CH=CH_2}$$
$$\begin{array}{ccc} \phi_1 & \phi_2 & \phi_3 \\ \phi_1^* & \phi_2^* & \phi_3^* \end{array}$$

$$\longrightarrow \underset{\text{IV}}{\overset{+}{C}H_2\text{-}CH=CH\text{-}\overset{-}{C}H\text{-}CH=CH_2}$$
$$\begin{array}{cccc} & \phi_1' & \chi_4 & \phi_3 \\ \chi_1 & \phi_1'^* & & \phi_3^* \end{array}$$

$$\longrightarrow \underset{\text{V}}{\overset{+}{C}H_2\text{-}CH=CH\text{-}CH=CH\text{-}\overset{-}{C}H_2} \qquad (2)$$
$$\begin{array}{cccc} & \phi_1' & \phi_2' & \chi_6 \\ \chi_1 & \phi_1'^* & \phi_2'^* & \end{array}$$

the orbital representation of this process can be given as follows (Scheme 2):[15)]



III_0 IV_0 V_0

Scheme 2.

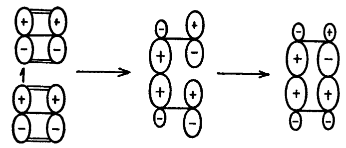
The first step, III→IV, is the same as that of I→II in Eq. 1, and the second step, IV→V, is equivalent to the reverse process, II→I, in Eq. 1. If these two steps(III→IV and IV→V) are included in one concerted process, *viz.*, the process III→V proceeds concertedly, the phase of χ_6 in V_0 should be dependent upon that of χ_1 (or χ_2). Each elementary step in Eqs. 1 and 2 can be considered to be a sort of nucleophilic substitution analogous to S_N2 reaction. Thus, the conversion of III to V may be a sequential nucleophilic substitution process. The phase correlation of AO's in such concerted processes as shown above can be expected to hold also for σ-systems.

In general, from a non-cyclic system (S_α) with n-two-center MO's (σ and/or π, n=2,3,4,$\cdots$) by sequential nucleophilic process, a new non-cyclic system (S_ω) can be obtained which is composed of an unoccupied nonbonding MO (χ_1) and an occupied nonbonding MO (χ_{2n}) in the two terminals, and of new $(n-1)$-two-center MO's between the two nonbonding MO's (*vide infra*). If this system forms a pericyclic system, the unoccupied orbital χ_1 should be situated in the position adjacent to the occupied orbital χ_{2n}. So long as the reaction proceeds concertedly, the phase of χ_{2n} is determind by that of χ_1. When the positive overlapping between χ_1 and χ_{2n} in S_ω is possible, an additional two-center bond is formed by χ_1 and χ_{2n}, making the pericyclic reaction allowable. On the other hand, when the overlapping between χ_1 and χ_{2n} is negative or antibonding, the two-center bond between the two terminals can not be formed, thus the reaction is forbidden.

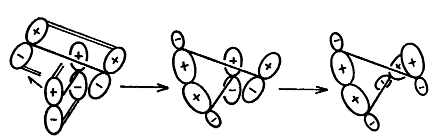
$$S_\alpha \xrightarrow{\text{Sequential Nucleophilic Process}} S_\omega$$
$$\begin{array}{ccccc} \phi_1 & \phi_2 & \phi_3 & \cdots\cdots & \phi_n \\ \phi_1^* & \phi_2^* & \phi_3^* & \cdots\cdots & \phi_n^* \end{array} \qquad \begin{array}{cccccc} & \phi_1' & \phi_2' & \cdots\cdots & \phi'_{n-1} & \chi_{2n} \\ \chi_1 & \phi_1'^* & \phi_2'^* & \cdots\cdots & \phi'^*_{n-1} & \end{array}$$

χ_1, χ_{2n} in S_ω	Pericyclic Rection
Bonding	Allowable
Antibonding	Forbidden

The phase relationship (bonding or antibonding) between χ_1 and $\chi_{2\omega}$ in S_ω should change according to the number and the relative configuration of the two-center bonds included in the pericyclic system. For example, when II_0 and V_0 are shown in the cis-bent form, it can easily be predicted that the reaction butadiene→cyclobutene is conrotatory, and that the reaction hexatriene→cyclohexadiene is disrotatory (Fig. 2).



(a) Parallel approach.



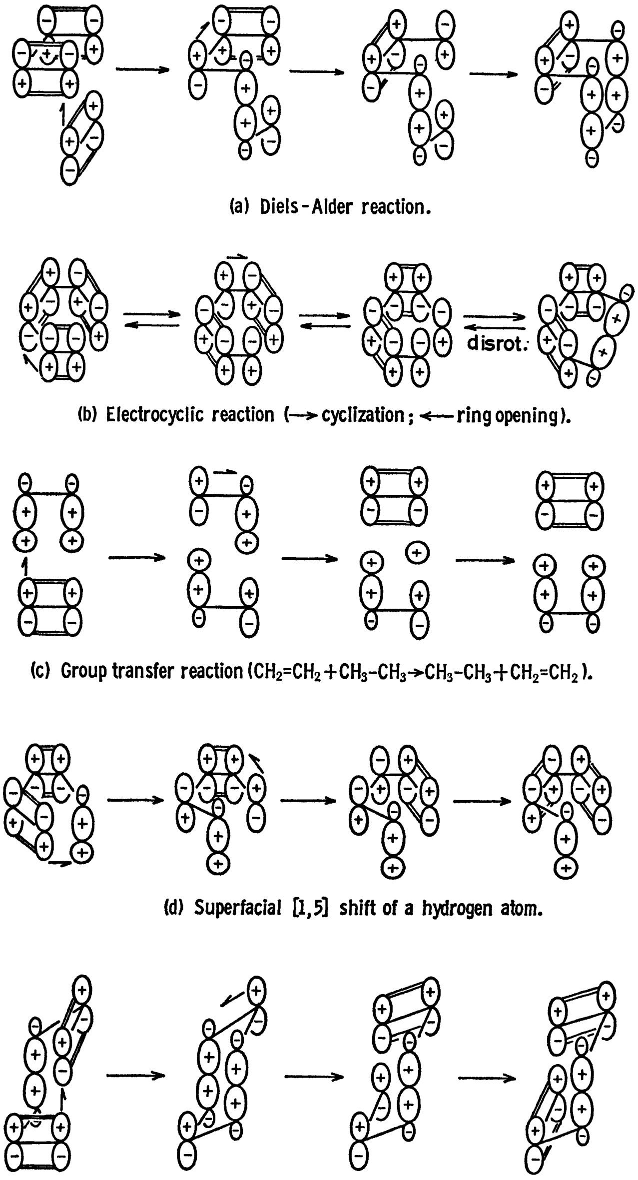
(b) Orthogonal approach.

Fig. 1. Mutual cycloaddition of ethylenes.

The analysis of reaction based on this argument is well demonstrated by the examples in Fig. 1. The mutual cycloaddition of ethylene in parallel approach gives the antibonding interaction between the terminals in the final step, which indicates that the reaction is forbidden. On the other hand, the bonding interaction between the terminals can be obtained in orthogonal approach, which means that the reaction is allowable. Other examples of allowed reactions are given in Fig. 2.

When the reaction system contains an odd number of AO's as in the case of carbanion or carbonium ion, the following treatment is reasonable.

System Involving an Occupied Nonbonding MO. In the following reaction,



(a) Diels-Alder reaction.

(b) Electrocyclic reaction (→ cyclization; ← ring opening).

(c) Group transfer reaction ($CH_2{=}CH_2+CH_3\text{-}CH_3 \rightarrow CH_3\text{-}CH_3+CH_2{=}CH_2$).

(d) Superfacial [1,5] shift of a hydrogen atom.

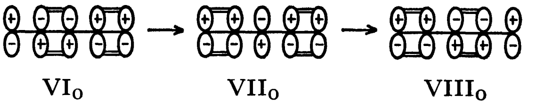
(e) Cope rearrangement (with chair-type transition state).

Fig. 2. Examples of allowed reaction.

$$\begin{array}{cccccc} \overset{-}{C}H_2\text{-}CH{=}CH\text{-}CH{=}CH_2 & & & \rightarrow & CH_2{=}CH\text{-}\overset{-}{C}H\text{-}CH{=}CH_2 & \\ \text{VI} & & & & \text{VII} & \\ \chi_0 & \phi_1 & \phi_2 & \phi_0' & \chi_2 & \phi_2 \\ & \phi_1^* & \phi_2^* & \phi_0'^* & & \phi_2^* \end{array}$$

$$\begin{array}{ccc} \rightarrow CH_2{=}CH\text{-}CH{=}CH\text{-}\overset{-}{C}H_2 & & \\ \text{VIII} & & \\ \phi_0' & \phi_1' & \chi_4 \\ \phi_0'^* & \phi_1'^* & \end{array} \qquad (3)$$

the orbital-array representations of each step are given as follows (Scheme 3):



VI_O $\qquad$ VII_O $\qquad$ VIII_O

Scheme 3.

Since the two ethylenic π-systems and one negative center in VI are regarded as being independent of each other, the phase of AO's between these three systems can be taken arbitrarily. Similarly to Eqs. 1 and 2, reaction VI→VII is initiated through the interaction between χ_0 and ϕ_1^*, two new two-center bonds and an occupied nonbonding center at another terminal being obtained in VIII.

In general, by sequential nucleophilic process, from a noncyclic system (S_α) consisting of an occupied nonbonding MO(χ_0, the lone-pair center) at the beginning terminal and n-two-center MO's(n=1,2,3……),[16] a new system (S_ω) can be obtained which is composed of new n-center MO's and a new lone-pair center (χ_{2n}) at the end terminal.

$$S_\alpha \xrightarrow{\text{Sequential Nucleophilic Process}} S_\omega$$

$$\begin{array}{llcl} \chi_0 \quad \phi_1 \quad \phi_2 \cdots\cdots \phi_n & & \phi_0' \quad \phi_1' \cdots\cdots \phi'_{n-1} & \chi_{2n} \\ \quad\;\; \phi_1^* \;\, \phi_2^* \cdots\cdots \phi_n^* & & \phi_0'^* \;\, \phi_1'^* \cdots\cdots \phi'^*_{n-1} & \end{array}$$

When this system forms a pericyclic system, the unoccupied orbital $\phi_0'^*(=\chi_0-\chi_1)$ is to be situated in the position adjacent to the occupied orbital χ_{2n}. So long as the reaction proceeds concertedly, the phase of χ_{2n} is determined by that of χ_0. Thus, if the positive overlapping between χ_{2n} and χ_0 in $\phi_0'^*$ is possible, χ_{2n} can interact with $\phi_0'^*$ in a bonding manner; in this case, this pericyclic reaction is allowable.

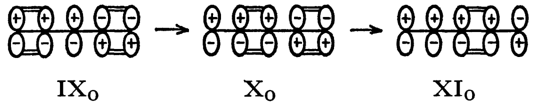
Alternatively, this type of reaction can be treated in the same way as that of systems with an even number of AO's by regarding χ_0 as a two-center MO with a ghost unoccupied AO. (*Cf. Participation of Lone-pair Orbital*).

System Involving an Unoccupied Nonbonding MO. In the following reaction,

$$\begin{array}{cccccc} CH_2{=}CH\text{-}\overset{+}{C}H\text{-}CH{=}CH_2 & & & \rightarrow & \overset{+}{C}H_2\text{-}CH{=}CH\text{-}CH{=}CH_2 & \\ \text{IX} & & & & \text{X} & \\ \phi_0 & & \phi_2 & & \phi_1 & \phi_2 \\ \phi_0^* & \chi_2 & \phi_2^* & \chi_0 & \phi_1^* & \phi_2^* \end{array}$$

$$\begin{array}{ccc} \rightarrow \overset{+}{C}H_2\text{-}\overset{+}{C}H\text{-}CH{=}CH\text{-}\overset{-}{C}H & & \\ \text{XI} & & \\ & & \phi_1' \quad \chi_4 \\ \chi_0 & \chi_1 & \phi_1'^* \end{array} \qquad (4)$$

the orbital-array representations of each step can be given as follows (Scheme 4):



IX_O $\qquad$ X_O $\qquad$ XI_O

Scheme 4.

As in the case of I_o, III_o, and VI_o, the phase of AO's between three systems (two ethylenic π-systems and one nonbonding center) in IX_o can be taken arbitrarily. The phase of the unoccupied nonbonding MO is adjusted to that of ϕ_0 so that the bonding interaction may arise between them in the process $\text{IX}_\text{o}\rightarrow\text{X}_\text{o}$; the treatment corresponds to that of each elementary step in Scheme 1—3. The first nucleophilic process

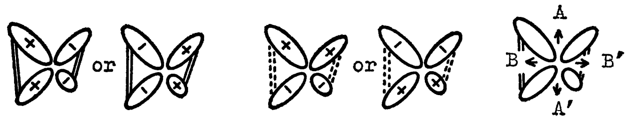
(IX→X) is not of substitution, and the second process (X→XI) is equivalent to I→II in Eq. 1.

For this type of reaction system, the following general, schematic expression can be given:[16]

$$
\begin{array}{ccc}
S_\alpha & \xrightarrow{\hspace{3em}} S_\alpha{}' \xrightarrow{\text{Seq. Nuc. Process}} & S_\omega \\
\phi_0 \quad \phi_2 \cdots \phi_n & \phi_1 \quad \phi_2 \cdots \phi_n & \phi_1{}' \cdots \phi'_{n-1} \; \chi_{2n} \\
\phi_{0*} \; \chi_2 \; \phi_2{}^* \cdots \phi_n{}^* & \chi_0 \; \phi_1{}^* \; \phi_2{}^* \cdots \phi_n{}^* & \chi_0 \; \chi_1 \; \phi_1{}'^* \cdots \phi'_{n-1}{}^*
\end{array}
$$

In the concerted process, the phase of χ_{2n} is determined by that of χ_0(or χ_1) in ϕ_0 of $S_\alpha(\phi_0=\chi_0+\chi_1)$. Therefore, when the positive overlapping between χ_0 and χ_{2n} in S_ω is possible, the pericyclic reaction is allowable.[17]

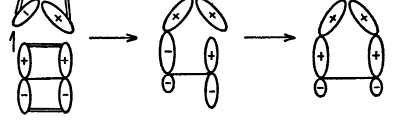
Cheletropic Reactions. Cheletropic reactions are a specific type of pericyclic reaction. As an example, the addition reaction of singlet carbene to ethylene is discussed. The carbene species has two localized MO's; one is occupied sp^2 (σ orbital) and the other unoccupied p(p orbital).[18] In order to avoid introducing a qualified nucleophilic and electrophilic center into the reaction process, these two orbitals are dealt with as their combination in terms of LCMO. Thus, the new bonding and antibonding MO are given as follows:



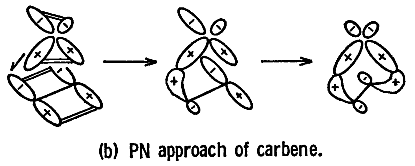
$\sigma+$p $\quad -(\sigma+$p) $\qquad \sigma-$p $\quad -(\sigma-$p)

Bonding MO $\qquad$ Antibonding MO

The bonding MO should be occupied, having its maximum extension in the direction of B; the antibonding MO should be unoccupied, having its maximum extension in the direction of A. Consequently, carbene species should direct side B toward the ethylene π system in its pseudo-nucleophilic(PN) approach to ethylene (*vide infra*), and side A toward the π system in its pseudo-electrophilic(PE) approach according to the HOMO-LUMO maximum overlapping principle.[19] In view of the fact that the extensions B-B′ and A-A′ can be considered alternatively to be the σ and the p MO of carbene, respectively, the merit of π approach of carbene in addition to olefin[20] can be interpreted easily.



(a) PE approach of carbene.



(b) PN approach of carbene.

Fig. 3. Addition of carbene to ethylene.

Thus, the addition of singlet carbene to ethylene can be illustrated as in Fig. 3, in which the MO's of carbene can be treated in the same manner as that of olefinic π MO.[21] The process through PE approach of carbene to ethylene is allowed, while the reaction through PN approach is impossible because of steric reasons though the process is formally allowed. By this MO representation, it can be easily understood that carbene functions in an antarafacial manner in PE approach, namely in non-linear cheletropic reaction, and that it acts in a suprafacial fashion in PN approach, namely in linear cheletropic reaction.

Interpretation of Secondary Effects. The secondary conformational effects in concerted cyclo-addition or sigmatropic reactions have been interpreted in terms of the HOMO-LUMO[1,2] or the NHOMO-NLUMO interaction.[2] The present approach can also provide an analogous interpretation for the effects. As an example, the endo selectivity in the Diels-Alder reaction of two butadiene molecules is explained in the following way (Fig. 4). The reaction is represented by the process: from C_6 to C_1, from C_2 to C_3, and from C_4 to C_5(C_6→C_1; C_2→C_3; C_4→C_5, Route I). An alternative process, however, can proceed via [C_2→C_7; C_6→C_1, (Route II)] to afford a four-membered cyclic transition species. In this transition species, C_4 and C_5 are still interactive, so that it changes to the Diels-Alder adduct *via* [C_4→C_5; C_8→C_7; C_2→C_3,

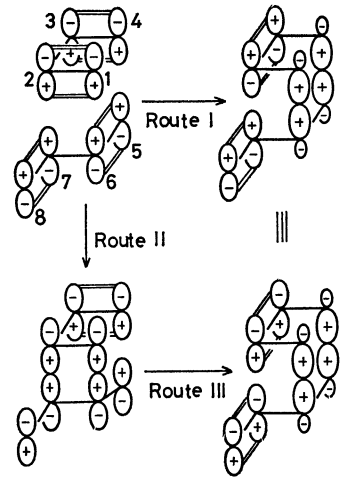


Fig. 4. Diels-Alder reaction of two butadiene molecules

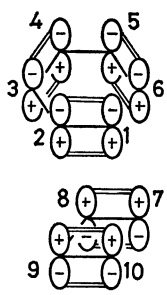


Fig. 5. MO representation of the endo approach of [4+6] cycloaddition between butadiene and hexatriene.

(Route III)]. That is to say, the MO bonding interaction, $C_2 \rightarrow C_7$ and $C_6 \rightarrow C_1$, may decrease the energy of the endo transition state, and promote the formation of cyclohexene ring. In contrast, in a [4+6] cyclo-addition (Fig. 5), an allowed process, $C_2 \rightarrow C_3$; $C_4 \rightarrow C_5$; $C_6 \rightarrow C_7$; $C_8 \rightarrow C_9$; $C_{10} \rightarrow C_1$, can be followed to give the [4+6] cyclo-adduct. However, an alternative process *via* $C_5 \rightarrow C_8$; $C_9 \rightarrow C_2$ is possible to give easily a six-membered cyclic transition species, in which the orbitals of C_1 and C_{10}, and of C_6 and C_7 become antibonding with each other, respectively. Consequently, the endo approach of the reactants may prevent the [4+6] cycloaddition. The preference of chair type transition state in the Cope rearrangement can be interpreted also in the same way.

Participation of Lone-pair Orbital to Pericyclic Systems. In nucleophilic non-cyclic concerted reactions with amines, the lone-pair orbital (n orbital) of nitrogen should function as the HOMO. When a hetero-atom such as nitrogen, oxygen, or halogen is contained in a pericyclic reaction system, its n orbital can also participate, at least formally, as a HOMO in the MO interaction.[22,23]

Isomerization of isoxazoline to *C*-acylaziridine[24] can be analyzed as an allowed [1,3] sigmatropic reaction with inversion at nitrogen. For this reaction, an alternative allowable process can be represented with participation of the nitrogen n orbital (Fig. 6), in which the configuration of nitrogen of the product is identical with that of the former process. By steric requirement, the latter process might be favorable. In this type of process, an n orbital should be regenerated with retention of orbital phase at the hetero-atom for allowed reactions (Fig. 6). By taking up the participation of 3p-n orbital of chlorine, a cyclic concerted scheme can be illustrated formally for S_Ni reaction of alkyl chlorosulfite.

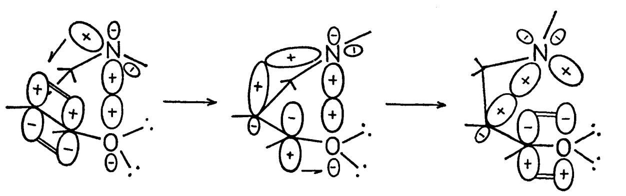
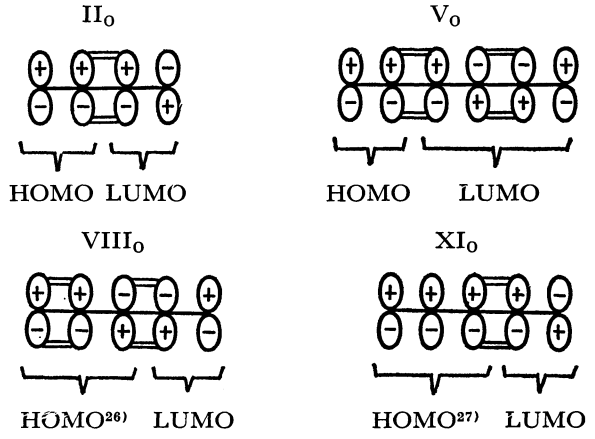


Fig. 6. Isomerization of isoxazoline to acylaziridine with participation of nitrogen lone-pair orbital.

Discussion

Pericyclic reactions in ground states can be followed by the present procedure (Fig. 2). The acutal reactions proceed neither stepwise nor via the so-called nucleophilic substitution scheme. However, according to Fukui, "a stepwise recognition of concerted reactions may be more reasonable than an attempt to understand each concerted multi-center reaction as a simultaneous change."[2] The feasiblity of stepwise recognition of concerted multi-center reactions might be related to the fact that delocalized MO's can be derived from localized MO's in terms of LCMO.[25] If a multi-center cyclic reaction proceeds concertedly, each consituent elementary step should be a concerted process (*vice versa*).

The orbital arrays of II_o, V_o, $VIII_o$, and XI_o are the same as those of the HOMO-LUMO interaction method (Scheme 1—4):



So far as the orbital phase alteration is concerned, the process through nucleophilic substitution scheme represents the delocalized LUMO: for example, in systems with an even number of AO's, the first nucleophilic process induces the localized HOMO to the localized LUMO, and the next and further processes will give the delocalized LUMO through the procedure corresponding to the LCMO method. This relationship can afford a theoretical ground to the present method.

Transformation between canonical forms of a conjugate system in classical molecular formula is to be taken as an intramolecular nucleophilic process. In Hückel systems, the two Kekulé formulas of [4N+2] annulene can be converted into each other by the present procedure, but not those of [4N] annulene; on the other hand, the principle should be the reverse in Möbius systems. This situation can give an alternative indirect reasoning for the present method in view of the aromaticity of transition state of pericyclic reactions in the Hückel-Möbius concept.[3,4]

Although the present method is somewhat roundabout, it can in a unified manner be applied also to the systems with low symmetry and to those in which the delocalized HOMO and LUMO can not easily be represented. This method is inapplicable to the systems with delocalized or three- or multi-center bonds. Since reaction systems are represented with localized MO's, the exact nature of molecules, especially of conjugate systems, can not be expressed. π and σ bonds are not differentiated from each other, and the analysis of reaction is carried out merely qualitatively. This method can not estimate the facility of reaction, but only whether a reaction can proceed concertedly or not.

For reactions in excited states, the present procedure does not afford any prediction, since it is based essentially on nucleophilic substitution process. Formally, however, a modification in which the antibonding representation is adopted for the initial nucleophilic center instead of the bonding one can give selection rules for reactions in excited states. This procedure corresponds to the SOMO-LUMO interaction scheme,[2] but has no theoretical grounds within the scope of the present consideration based on nucleophilic processes.

References

1) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed.*, (*Engl.*), **8**, 781 (1969); "The Conservation of Orbital Symmetry," Academic Press, New York (1969).

2) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

3) H. Zimmerman, *ibid.*, **4**, 272 (1971).

4) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

5) H. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972).

6) It has been shown by Fukui that a concerted multicenter reaction can be treated as a combination of two two-center interactions in the HOMO-LUMO interaction method. (See Ref. 2).

7) W. A. Goddard III, *J. Amer. Chem. Soc.*, **92**, 7520 (1970); **94**, 793 (1972).

8) This type of reaction has also been explained MO-theoretically. (See Ref. 2.)

9) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York (1960), p. 492.

10) S_N2 reactions treated MO-theoretically have been reported. *Cf.* (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York (1961), p. 367; (b) K. Fukui, "Modern Quantum Chemistry," Vol. I, ed. by O. Shinanoglŭ, Academic Press, New York (1965), p. 49.

11) The charge transfer from ϕ_1 to $\phi_2{}^*$ will cause weakening of both bonds.

12) "The total stabilization energy (ΔW) of a chemically-interacting state in a reaction between two systems is given by Coulombic (E_Q), exchange (E_K), delocalization (D), and polarization(π) terms as follows:

$$\Delta W = E_Q - E_K - D - \pi$$

D is the stabilization energy due to the mixing in of the charge-transferred states; it works to promote the reaction. The last term is also the stabilization energy, but less important." *Cf.* K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989(1968).

13) There is no orbital-phase relationship between ϕ_1 and ϕ_2 before the reaction. Once the reaction proceeds concertedly, the relationship develops throughout all orbitals that take part in reaction.

14) In general, two or more alternative representations of orbital arrays of the localized bonding MO are possibile for a conjugate system, each giving the same result. The orbital phase of the antibonding MO is so chosen that the bonding interaction may arise in the process analogous to nucleophilic substitution.

15) Three orbital representations are possible for the bonding level of III, each giving the same result(V_o).

16) It is possible in any system of this type to arrange the nonbonding center and two-center bonds in this manner.

17) $n=1,2,3,\cdots\cdots$. When $n=1$, χ_0 should be bonding to χ_2 in ϕ_1 of $S_{\alpha'}$ in the allowed reaction as a matter of course.

18) W. Kirmse, "Carbene Chemistry," 2nd Ed., Academic Press, New York (1971), p. 165.

19) As for this principle, see Ref. 2.

20) Ref. 18, p. 281.

21) Intra- and intermolecular insertion reactions of carbene also can be analyzed easily with the present MO representation.

22) The role of a localized vacant orbital such as the 2p orbital of boron has been pointed out by Fukui. *Cf.* K. Fukui, This Bulletin, **39**, 498 (1966).

23) The possibility of such participation of lone-pair orbital as well as low-lying unoccupied orbital of heteroatom has been mentioned by Woodward and Hoffmann. *Cf.* Ref. 1.

24) I. Adachi, K. Harada, R. Miyazaki, and H. Kano, *Chem. Pharm. Bull.* (Tokyo), **22**, 61 (1974).

25) For example, the process III→V can be considered to be the delocalization process of a conjugate system.

26) Although this orbital array is not correct for the HOMO of allyl anion, it can be assigned to the HOMO for allyl anion due to the fact that this representation has nodal properties similar to that of the correct one.

27) HOMO of allyl cation.