Orbital Tilting and Hybridization Change. An Illustrational Molecular Orbital Approach to an Addition ($CH_2=CH_2+HBr \rightarrow CH_3CH_2Br$) and an Elimination Reaction ($CH_3CH_2Br/Base \rightarrow CH_2=CH_2$)

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Configuration alteration and hybridization change in the addition of hydrogen bromide to ethylene and those in its reverse, E2-type reaction were illustrated in terms of orbital tilting on the basis of the concept of stabilizing and destabilizing second order orbital interactions. The predominancy of trans fashion in these reactions are also visualized qualitatively.

As has been seen in the symmetry rule of Woodward and Hoffmann,1) and the frontier orbital method of Fukui,2) non-computational molecular orbital treatments, in spite of being qualitative, have been proved to be powerful and extremely useful for predicting pericyclic reactions. Furthermore, various phenomena in organic chemistry, such as molecular geometries and reactivities, are also explained successfully by using molecular orbitals represented qualitatively.3) Thus, non-computational and qualitative MO-approaches deserve consideration in its own right, and may be attractive from the standpoint of organic chemistry.

In recent years, Fukui and his co-workers4) have first illuminated MO-theoretically the stereochemistry of 1,2-addition reactions in olefinic systems and that of E2 reactions.5) In their treatment, for example, in the addition to an olefin, originally orthogonal, delocalized σ- and π-MO's are mixed through the orbital interactions with a third orbital located in the molecule of an attacking reagent: these orbital interactions result in new bond formation and hybridization change, and the nuclear movement of four substituents in the ethylenic moiety, that is, the configuration alteration, is taken concomitantly into consideration.

The orbital distortion technique described by Burgess and Liotta6) for predicting the stereochemical courses of organic reactions involves also this type of second order σ-π orbital mixing, but makes no mention of overall hybridization change.

On the other hand, by Woodward and Hoffmann,1) cyclizations of conjugated polyenes such as that of *s-cis*-butadiene to cyclobutene have been represented in terms of the rotation or inclination of both terminal methylenes. These types of reactions can be understood to be configuration alteration and hybridization change roughly at the two terminal methylenes. The inclination of methylene groups implies tilts of orbitals located in these groups, and the shifts of hydrogen nuclei of terminal methylenes can be recognized unequivocally.7) It should be noted that the inclination of methylene groups, that is, the tilt of orbitals can be explained in terms of HOMO-LUMO orbital interactions between the two π systems which divide formally a conjugated polyene into two olefinic parts.2)

The concept of tilt of orbitals has appeared also in the interpretation of substituent angles in π-bonding systems of metal complexes8) and in the elucidation of non-planarity in π-systems of norbornene9,10) and *syn*-sesquinorbornene:11) in norbornene and *syn*-sesquinorbornene, tilts of orbitals have been introduced in terms of hyperconjugative orbital interactions.

In the present paper, on the basis of the concept of stabilizing two-electron and destabilizing four-electron orbital interactions, an attempt to illustrate configuration alteration and hybridization change in the title reactions is made by the procedure of orbital tilting.

Results

Addition of Hydrogen Bromide to Ethylene. For this reaction (Eq. 1), we set a situation in which an incoming proton approaches to one methylene carbon perpendicularly to the molecular plane of ethylene in the initial step of reaction.12)

$$\underset{(C^1\quad C^2)}{CH_2{=}CH_2} + HBr \rightarrow CH_3CH_2Br \qquad (1)$$

When the interactions between the 1s orbital of proton and σ ones located in the C–H bond regions of ethylene are neglected as a first approximation,13) π, π^*, σ_{CC}, σ^*_{CC} (these MO's are given by the linear combination of basis 2p AO's, p_1 and p_2, and of sp^2 hybrids, r_1 and r_2, which are located in C^1 and C^2), and the 1s orbital of the incoming proton (H^+) should be considered for the reaction system: for the energies of these orbitals (π, π^*, σ_{CC}, and σ^*_{CC}), the values of an SCF-MO calculation14) in the literature may be referred to,15) and the ionization potential of hydrogen16) can be assigned to that of the 1s orbital of proton (Table 1).

On approach of H^+ to C^1, the proton 1s orbital interacts with π, π^*, σ_{CC}, and σ^*_{CC}; thus, the originally orthogonal π- and σ-bond orbitals interact through the 1s orbital. The orbital interaction principle based on the perturbation theory17) tells that orbital interactions can be treated pairwise or stepwise when

Table 1. The Orbital Energies for Reference to Orbital Interactions

Molecule or Ion	Orbital	Energy/eV
H^+	1s	−13.60
C_2H_4	π^*	6.60
	π	−10.09
	σ^*_{CC}	17.40
	σ_{CC}	−15.28
t-BuO$^-$	n	−10.47
C_2H_5Br	σ^*_{CH}	17.83
	σ_{CH}	−17.40
	σ^*_{CBr}	2.29
	σ_{CBr}	−13.54
	σ^*_{CC}	15.56
	σ_{CC}	−13.29

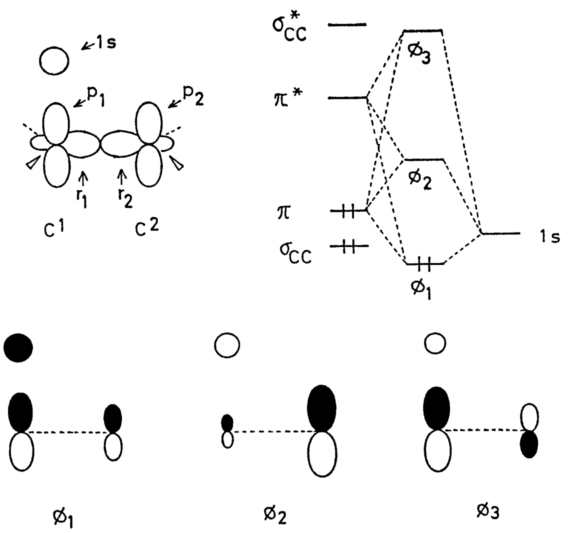

Fig. 1. Three-center orbitals from π, π^*, and 1s.

an orbital level interacts with several others; therefore, a set of semi-delocalized three-center orbitals (ϕ_1, ϕ_2, ϕ_3) can be pictured from π, π^*, and 1s in the first step ($\phi_1=\pi+1s+\pi^*$, $\phi_2=\pi-1s-\pi^*$, $\phi_3=\pi^*-1s+\pi$) (Fig. 1). Delocalized orbitals for the initial stage of reaction are represented by the interactions of σ_{CC} and σ^*_{CC} with ϕ_1, ϕ_2, and ϕ_3 in the second step.

Trans Addition: According to the frontier orbital theory, a chemically interacting system is stabilized when HOMO-LUMO interactions are realized; thus, the interaction between ϕ_1 (HOMO of the semi-delocalized three-center orbital system) and σ^*_{CC} (σ-LUMO) and that between σ_{CC} (σ-HOMO) and ϕ_3 (NLUMO of the semi-delocalized three-center system) stabilizes the reaction system under consideration. In the initial stage of reaction, the orbital fractions located in C^1 lying closer to the proton must be perturbed more strongly and should play a significant role in the change of hybridization. The orbital amplitude of ϕ_2 (LUMO of the semi-delocalized three-center system) in C^1 is very small; thus, ϕ_2 makes little contribution to hybridization change. Therefore, ϕ_3, instead of ϕ_2, should be taken into consideration for the orbital interaction leading to hybridization change. Level ϕ_2 is virtually nonbonding and will grow into LUMO of transient $C_2H_5^+$ species in the course of orbital interaction.

The in-phase combinations between ϕ_1 and σ^*_{CC} and between σ_{CC} and ϕ_3 are shown in Fig. 2. The signs of combination of orbitals are referred to the phase of fraction 1s in ϕ_1 or ϕ_3 and that of the predominant lobe of fraction r_1 in σ^*_{CC} or σ_{CC}.[18] In this situation, when the methylene group (C^1H_2) lying closer to the approaching proton inclines in the symmetrically bisecting plane (with respect to C^1H_2) to the configuration in which the two methylene hydrogenes are remote from the incoming proton, together with the synchronous inclination of the other methylene group (C^2H_2) in the same direction (syn-inclination), antibonding entities involved in $[\phi_1+\sigma^*_{CC}]$ and $[\sigma_{CC}+\phi_3]$ are decreased and increased in-phase orbital overlaps are realized by orbital tilting (Fig. 2). The resulting MO-representations are related to the qualitative delocalized occupied levels of transient $C_2H_5^+$ species[19] and have their predominant extensions in the new C-H and C-C σ bond regions, respectively.

The MO-representation of LUMO level for the $C_2H_5^+$ species can be obtained by orbital mixing, $\phi_2+\sigma^*_{CC}-\sigma_{CC}$, and by subsequent orbital tilting: the sign of combination should be selected in such a way that fraction r_1 in σ^*_{CC} and fraction p_2 in ϕ_2 are in-phase throughout the course of orbital tilting, since the amplitude of fraction p_2 is greater than that of fraction p_1 in ϕ_2 (Fig. 2). The delocalized LUMO of transient $C_2H_5^+$ species thus obtained has its predominant extension in the location of C^2 and in the trans side to the incoming proton across the central bond. This preeminent extension of LUMO level in the trans side means trans preference in the stereochemical course of the addition reaction.[4]

Cis Addition: The orbital interaction principle[17]

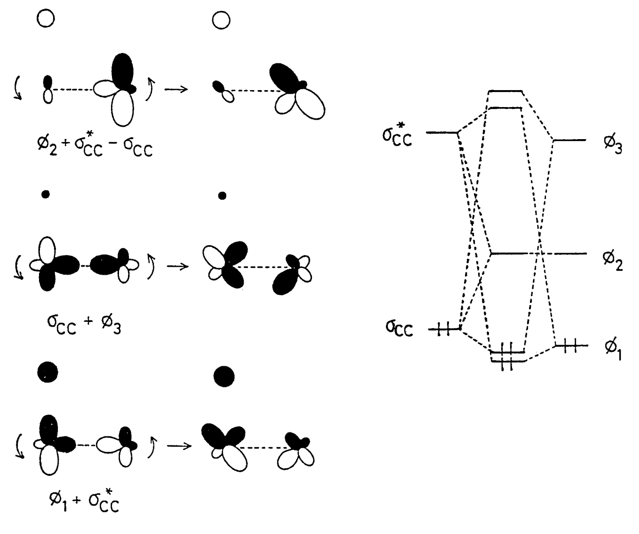

Fig. 2. Orbital interaction and tilting in the addition reaction (trans mode).

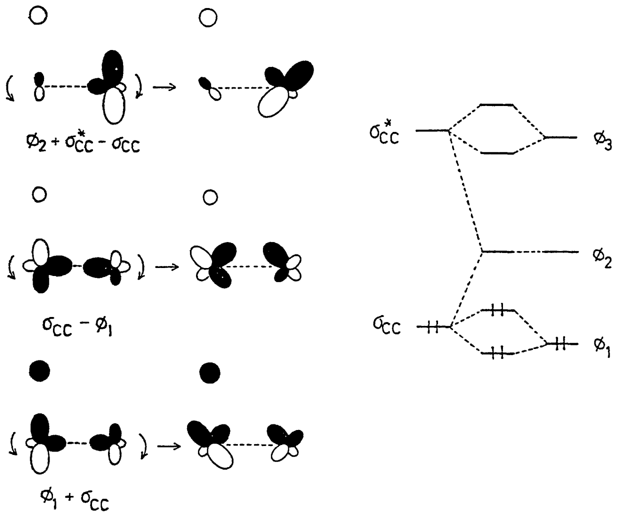

Fig. 3. Orbital interaction and tilting in the addition reaction (cis mode).

describes also that the interaction between two occupied levels destabilizes a chemical system. Figure 3 shows this type of interaction set to the reaction under consideration. The interaction between ϕ_1 and σ_{CC} yields a lower level ($[\phi_1+\sigma_{CC}]$) and a higher one ($[\sigma_{CC}-\phi_1]$). Since the destabilization of the original higher level (σ_{CC}) is, in general, always slightly larger than the stabilization of the lower level (ϕ_1), this type of interaction is energetically unfavorable. However, when the methylene groups (C^1H_2 and C^2H_2) incline synchronously to the configuration in which the four methylene hydrogens are remote from the incoming proton (anti-inclination), antibonding entities involved in these combinations may be reduced and their bonding characters must be increased by orbital tilting; thus, the reaction system is stabilized (Fig. 3). Evidently, such stabilization as gained by HOMO-(N)LUMO interaction in the syn-inclination can not be expected in this case. The resulting orbitals represent qualitatively the semi-delocalized occupied levels of the transient $C_2H_5^+$,[20] and have their predominant extension in the new C-H and C-C σ bond regions, respectively.

The delocalized LUMO of transient $C_2H_5^+$ in the anti-inclination can be represented in a similar manner as in the syn-inclination by orbital tilting of combination $[\phi_2+\sigma^*_{CC}-\sigma_{CC}]$: in this case, the sign of combination should be selected in such a way that fraction r_1 in σ^*_{CC} and fraction p_2 in ϕ_2 are in-phase throughout the course of orbital tilting. The resulting MO-representation has its predominant extension in the cis side in the location of C^2 (Fig. 3), which refers to the stereochemical course of the addition reaction in cis mode.

Elimination of Hydrogen Bromide from Ethyl Bromide. The potassium t-butoxide-induced 1,2-elimination of hydrogen bromide from ethyl bromide (Eq. 2) may be one of the most simple E2-type reactions.

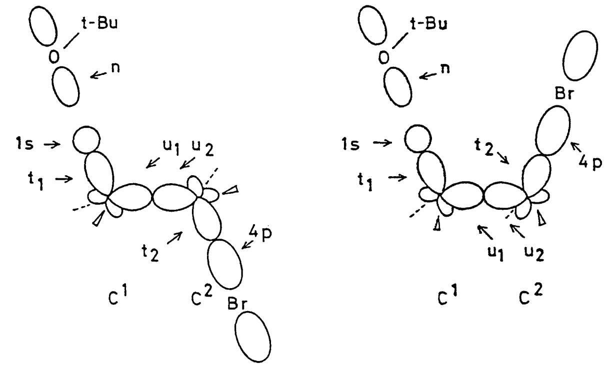

Fig. 4. Orbital locations of EtBr in the trans (left) and cis periplanar conformation (right) together with t-BuO$^-$.

$$\underset{(C^1\ \ C^2)}{CH_3CH_2Br}\xrightarrow[t\text{-}BuO^-]{-HBr}CH_2{=}CH_2 \qquad (2)$$

The reaction involves the abstraction of a 1-proton by base and the concerted departure of halide anion.[5] In order to achieve maximum overlap in developing bond orbitals, the orbitals related to new bond formation must all lie in one plane; thus, the arrangement of a 1-hydrogen and halogen to be eliminated should be trans or cis periplanar. When the interactions of localized orbitals related to the four out-of-periplanar C-H bonds of ethyl bromide are neglected as a first approximation, MO's σ_{CH}, σ^*_{CH}, σ_{CC}, σ^*_{CC}, σ_{CBr}, σ^*_{CBr} (these MO's are given by the linear combinations of basis 1s AO of 1-H, sp^3 hybrids located in C^1 and C^2 (t_1, u_1, t_2, u_2), and 4p AO of Br), and the nonbonding orbital (n) located in t-BuO$^-$ should be taken into consideration (Fig. 4). When the perturbational concept is applied to ethyl bromide, this molecule can be regarded as a union[21] between methane and methyl bromide; thus, the energies of σ_{CH}, σ^*_{CH}, σ_{CBr}, and σ^*_{CBr} can be estimated from those of appropriate orbitals in these molecules.[22] For the σ_{CC} and σ^*_{CC} levels of the molecule under consideration, ethane will be more adequately referred to than ethyl bromide in which σ_{CC} orbitals are perturbed by C-Br bond orbitals.[23] The ionization potential of t-butanol[24] may be made referrence to for the energy of n level in t-butoxide anion[25] (Table 1).

On approach of t-BuO$^-$ to 1-H, the n obital of t-BuO$^-$ begins to interact with σ_{CH} and σ^*_{CH} in the initial stage of reaction, and originally orthogonal σ-bond orbitals located in C^1-H, C^1-C^2 and C^2-Br interact through the participation of n orbital. On the basis of the orbital interaction principle,[17] let us consider the interaction among σ_{CH}, σ^*_{CH}, and n in the first step; then, a semi-delocalized three-center four-electron orbital system (ψ_1, ψ_2, and ψ_3) are obtained by the linear combination of σ_{CH}, σ^*_{CH}, and n ($\psi_1=\sigma_{CH}+n+\sigma^*_{CH}$, $\psi_2=n-\sigma_{CH}+\sigma^*_{CH}$, $\psi_3=\sigma^*_{CH}-n+\sigma_{CH}$)[26] (Fig. 5).

Trans Elimination: In the trans-periplanar conformation, the orbital interaction between the three-center system and the localized two-center orbitals extended to the C^2–Br bond region (σ_{CBr} and σ^*_{CBr}) gives a new five-center orbital system in the second step. Since level ψ_2 lies close to σ_{CBr} and σ^*_{CBr} and the amplitude of fraction t_1 in ψ_2 is superior to that in ψ_1 and that in ψ_3, the NHOMO, HOMO, and LUMO level (ε_2, ε_3, and ε_4) of the semi-delocalized five-center system can be represented approximately as $[\sigma_{CBr}+\psi_2+\sigma^*_{CBr}]$ ($=\varepsilon_2$), $[\psi_2-\sigma_{CBr}+\sigma^*_{CBr}]$ ($=\varepsilon_3$), and $[\sigma^*_{CBr}-\psi_2+\sigma_{CBr}]$ ($=\varepsilon_4$) by neglecting the participation of ψ_1 and ψ_3. The signs of combinations are based on the phase-relationship between the major lobe of fraction t_1 in ψ_2 and the minor lobe of fraction t_2 in σ_{CBr} and σ^*_{CBr} (Fig. 6).

In this situation, the HOMO-LUMO interactions between the five-center orbital system and the C–C σ orbital one (σ_{CC} and σ^*_{CC}) can be considered.

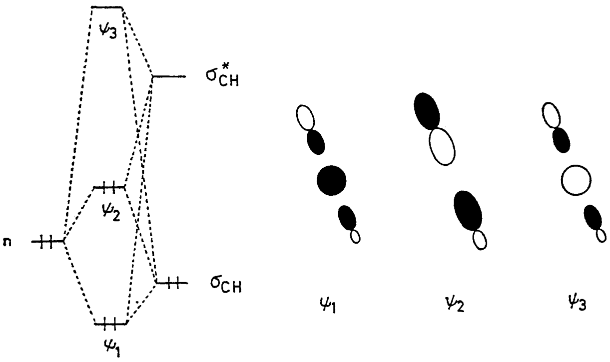

Fig. 5. Three-center orbitals from σ_{CH}, σ^*_{CH}, and n.

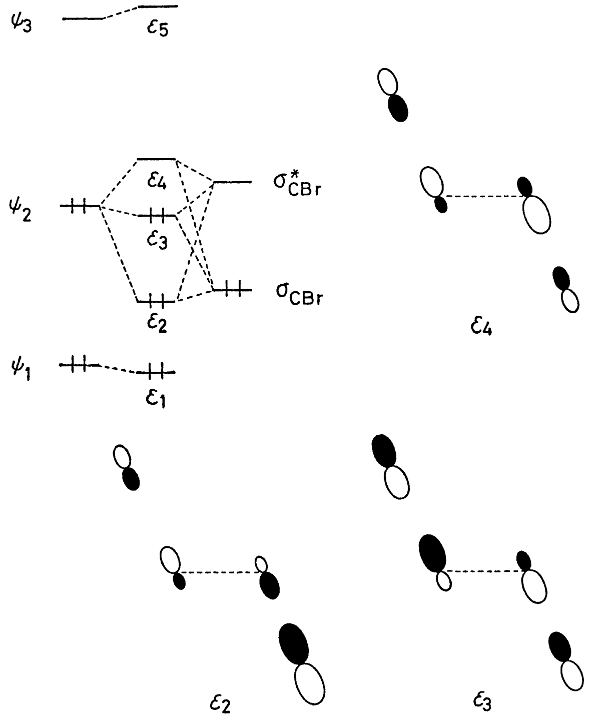

Fig. 6. Five-center orbitals from ψ_1, ψ_2, ψ_3, σ_{CBr}, and σ^*_{CBr} in the trans periplanar conformation.

In view of the local symmetry of orbitals, two sets of interactions, the interaction between ε_3 and σ^*_{CC} and that between ε_4 and σ_{CC} are available: both of them are in a stabilizing two-electron mode. The delocalized seven-center orbital representations, $[\varepsilon_3+\sigma^*_{CC}]$ and $[\sigma_{CC}+\varepsilon_4]$, are given in Fig. 7.[27] In these combinations, further stabilization arises from the inclination of the two methylene groups in the symmetrically bisecting plane to the configuration with the respective increasing proximity of four methylene hydrogens to the leaving 1-H and 2-Br (syn-inclination) in such a way that the four methylene hydrogens and the two carbon atoms lie in one plane, because an increased in-phase and a decreased out-of-phase orbital overlap are realized in the C–C π- and σ-bond regions by orbital tilting (Fig. 7). The resulting MO-representations are related to the π and σ_{CC} levels of ethylene molecule produced, and the counterparts, tilted $[\sigma^*_{CC}-\varepsilon_3]$ and $[\varepsilon_4-\sigma_{CC}]$, are to σ^*_{CC} and π^*. Level ε_2 will grow into the nonbonding orbital of leaving Br^-, while levels ε_1 and ε_5 develop into σ_{OH} and σ^*_{OH} located in a resultant *t*-BuOH, respectively.

Cis Elimination: For the cis-periplanar conformation, an alternative five-center six-electron orbital system (η_1—η_5) can be pictured by the combination of ψ_1, ψ_2, ψ_3, σ_{CBr}, and σ^*_{CBr} in a similar manner, in which η_2 (NHOMO) is given approximately as $[\sigma_{CBr}+\psi_2+\sigma^*_{CBr}]$, η_3 (HOMO) as $[\psi_2-\sigma_{CBr}+\sigma^*_{CBr}]$, and η_4 (LUMO) as $[\sigma^*_{CBr}-\psi_2+\sigma_{CBr}]$ (Fig. 8).

In this situation, two sets of interations, the interaction between η_3 (HOMO) and σ_{CC} and that between η_4 (LUMO) and σ^*_{CC}, are available in view of the symmetry of orbitals. The former interaction is in a destabilizing four-electron mode: thus, this type of interaction is energetically unfavorable. However, secondary stabilization arises from the inclination of two methylene groups to the configuration with increasing proximity of four methylene hydrogens to leaving 1-H and 2-Br (anti-inclination) because of an increased in-phase orbital overlap in $[\eta_3\pm\sigma_{CC}]$ by orbital tilting

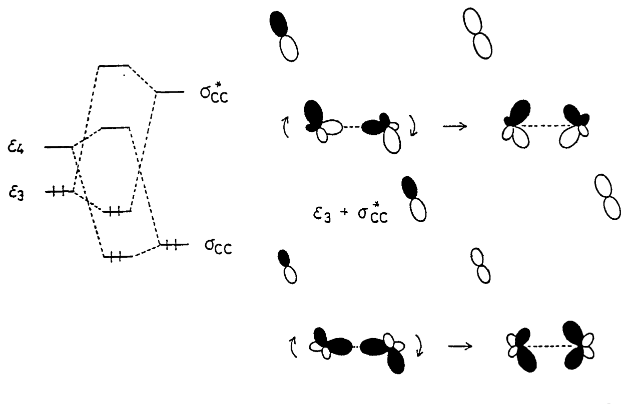

Fig. 7. Orbital interaction and tilting in the trans elimination.

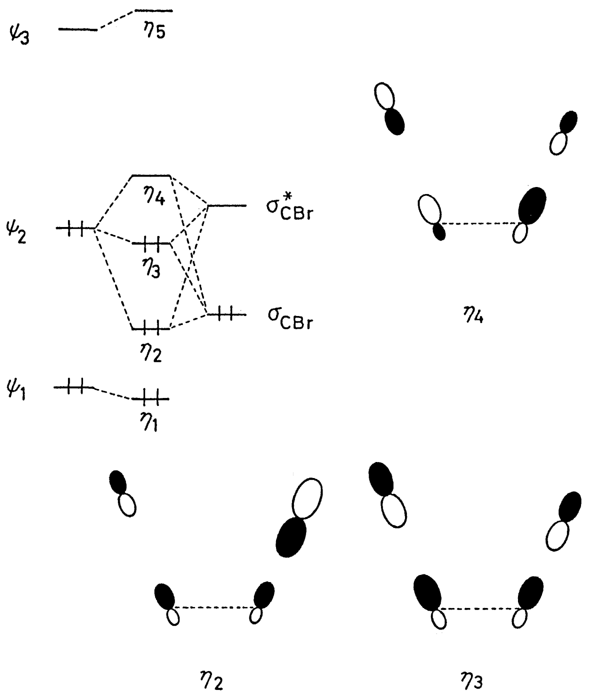

Fig. 8. Five-center orbitals from ψ_1, ψ_2, ψ_3, σ_{CBr}, and σ^*_{CBr} in the cis periplanar conformation.

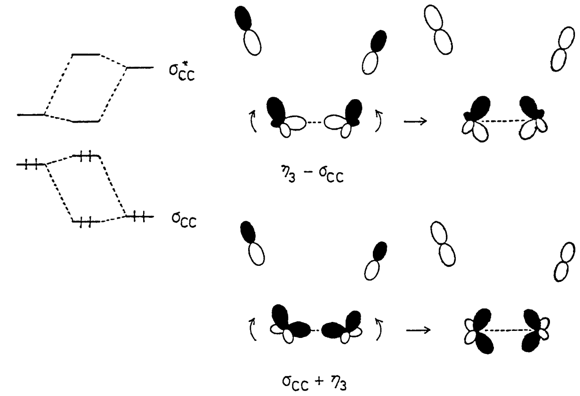

Fig. 9. Orbital interaction and tilting in the cis elimination.

(Fig. 9). The resulting MO-representations are related to the σ_{CC} and π levels of ethylene molecule, and tilted $[\eta_4 \pm \sigma^*_{CC}]$ are to π^* and σ^*_{CC}. Level η_2 will grow into the nonbonding orbital of leaving Br^-, while levels η_1 and η_5 correspond to the developing σ_{OH} and σ^*_{OH} located in *t*-BuOH respectively.

Discussion

Organic reactions may be referred to nuclear configuration alteration, which is induced by orbital interactions. In other words, reactions can be seized as transformations of some orthogonal molecular orbital systems into other new orthogonal ones from the viewpoint of orbital interaction concept. The new orthogonal orbital systems are generally generated by orbital mixing. However, in special cases, a new orthogonal system can be obtained approximately by a simple operation, tilts of orbitals. The cyclization of *s-cis*-butadiene to cyclobutene may be a typical example of these cases: the conrotation of terminal methylenes is explained in terms of the HOMO-LUMO maximum overlapping principle.[2] The C-H bonds of terminal methylenes are conserved throughout the reaction; thus, the rotation of terminal methylenes accompanied by the shifts of hydrogen nuclei gives a new orthogonal orbital system in this case.

A similar consideration of tilts of orbitals based on the concept of stabilizing two-electron and destabilizing four-electron orbital interaction may be applicable to some other types of reactions (intermolecular reactions), and has been focused on the title reactions in the present paper.[28]

As has been seen above, configuration alteration in the addition of hydrogen bromide to ethylene could be illustrated qualitatively by the procedure of orbital tilting. In addition, the trans-dominancy of reaction has been also represented: that is, the inclination of two methylene groups in the same direction (syn-inclination) is energetically advantageous to this reaction. As a general rule, trans fashion may be favorable to these types of reactions. However, syn-inclination is forbidden in rigid systems such as norbornene and acenaphthylene, because their two ethylenic carbons and the two substituents (e.g., C^1 and C^4 of norbornene) fixed in a cis mode should lie in one plane throughout the course of reaction. In such cases, anti-inclination will be forced to be selected; thus, the reaction should proceed in a cis manner as have been observed in norbornene[29] and acenaphthylene.[30]

The orbital tilting procedure could display also configuration alteration in the base-induced formation of ethylene from ethyl bromide, in which the trans elimination of hydrogen bromide is shown to be advantegeous energetically. In the reaction via the trans-periplanar conformation, the in-phase combination between ε_3 and σ^*_{CC}, $[\varepsilon_3+\sigma^*_{CC}]$ shown in Fig. 7, is essentially antibonding; however, it gains a great bonding character among the local orbitals located in C^1 and C^2 by orbital tilting. The resultant stabilization can be considered to contribute to the progress of reaction to a significant extent. In the cis-periplanar conformation, on the other hand, the corresponding combination, $[\eta_3-\sigma_{CC}]$ shown in Fig. 9, has a significant bonding character and gains only a certain addition by orbital tilting. Thus, much stabilization cannot be expected in this case. In a system such as 2-exo-bromonorbornene, however, only a cis-periplanar conformation is available between a β-hydrogen and the halogen to be removed. In such a case, the reaction should proceed in a cis manner.[31]

New basis hybrids for localized two-center bond orbitals of ethyl bromide and ethylene generated from the above reactions can be obtained by re-hybridiza-

Table 2. CNDO/2 Molecular Orbital Calculations on Reaction $[H^1H^2C^1{=}C^2H^3H^4 + H^+ \longrightarrow (H^1H^2H^5C^1{-}C^2H^3H^4)^+]$[a)]

Angle of inclination/°		0	10	20	30	45
Total energy/eV[b)]		−475.97	−476.22	−476.26	−476.09	−475.41
			(−476.17)	(−476.15)	(−475.91)	(−475.17)
Total valence electron energy/eV[b)]		−410.20	−410.66	−410.98	−412.24	−411.40
			(−410.14)	(−410.02)	(−409.88)	(−409.66)
LUMO energy/eV[b)]		−7.99	−8.04	−8.19	−8.39	−8.79
			(−8.08)	(−8.25)	(−8.47)	(−8.85)
Coefficients of LUMO in C^2 and H^5 (Syn-incl.)	$2p_z$	0.832	0.840	0.838	0.830	0.807
	$2p_x$	−0.135	−0.150	−0.164	−0.177	−0.192
	2s	0.055	−0.014	−0.083	−0.149	−0.234
	1s	−0.490	−0.472	−0.452	−0.430	−0.400
Coefficients of LUMO in C^2 and H^5 (Anti-incl.)	$2p_z$		0.833	0.836	0.827	0.806
	$2p_x$		−0.086	−0.037	0.010	0.073
	2s		0.120	0.179	0.231	0.293
	1s		−0.471	−0.448	−0.422	−0.383

a) Bond length (in Å): 1.438 (C-C), 1.086 ($C{-}H^{1,2,3,4}$), 1.160 ($C^1{-}H^5$). Bond angle (in °): 117.6 ($H^1{-}C^1{-}H^2$, $H^3{-}C^2{-}H^4$), 90 ($H^5{-}C^1{-}C^2$). Angle of inclination is the dihedral angle between plane $H^1{-}C^1{-}H^2$ or $H^3{-}C^2{-}H^4$ and the original molecular plane of ethylene. Interatomic distances (in Å, syn-inclination, 30°): 1.784 ($H^5{-}H^{1,2}$), 2.312 ($H^5{-}H^{3,4}$); (anti-inclination, 30°): 1.784 ($H^5{-}H^{1,2}$), 2.580 ($H^5{-}H^{3,4}$). b) Values in parentheses are those in the anti-inclination.

tion of the basis hybrids in the delocalized orbitals represented by orbital tilting;[32)] however, the new hybrids deviate from the normal state, sp^3- or sp^2-hybridization. These deviations must arise from neglecting the interactions of σ-orbitals located in the other C–H bond regions, but is not serious in view of the scope of qualitative approach. Neglecting the interactions of methylene σ-orbitals may be equivalent to regarding a methylene group as a "pseudo atom" bearing two restrictively directional atomic orbitals.

Orbital tilting does not mean the physical inclination of orbitals, but is merely an artificial device in analogy with orbital hybridization. The present procedure in which configuration alteration and the resulting hybridization change are treated concurrently by the aid of localized or semi-delocalized MO-representations with basis hybrid orbitals may make an easy recognition of chemical courses possible. Orbital tilting is specified in such a way that the HOMO-LUMO maximum overlap and the diminished antibonding entities in occupied levels may be realized; therefore, it can be said that the present approach has its theoretical grounds in the frontier orbital or the perturbation theory.

Appendix

For the purpose of confirming the present approach, CNDO/2 molecular orbital calculations[33)] were carried out on the reaction between an ethylene molecule and a proton.

Since the interaction of proton 1s with π and π* orbital of ethylene should decrease the π-electron density between carbon atoms, the C–C bond of ethylene molecule will be lengthened. Thus, the mean value (1.438 Å) of C–C bond lengths in ethylene and ethane was used tentatively for calculation. In the above-mentioned perpendicular approach of proton to C^1, the total energy of the reaction system is minimized when the interatomic distance between H^+ and C^1 is 1.160 Å. In this situation, the inclination of each methylene group holding their bond angles (H–C–H) constant and the H^+–C–C plane-symmetry was considered. The results of calculations are listed in Table 2.

As shown in Table 2, the syn-inclination stabilizes the reaction system to a greater extent than the anti mode does: the difference in the total energy and the total valence electron energy are 0.18 and 2.36 eV (4.1 and 54.4 kcal mol^{-1}) at 30°, respectively. In addition, the inclinations in both modes lead to a lowering of LUMO level, an increase in the orbital extension at C^2 (to the trans side in the syn mode and to the cis side in the anti-mode), and a decrease in the extension at the interacting H^+. These data may support the results of the qualitative approach described above.

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5) The predomonancy of trans fashion in 1,2-addition reactions in olefinic systems and that in E2 type reactions have been well established in many experimental results. These stereospecificities, in the classical organic chemistry, were elucidated or attempted to elucidate by relating the chemical courses to S_N2 reactions (for a reference, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York (1959), pp. 478 and 514). Furthermore, hybridization change accompanied by these reactions has been dealt with merely perfunctorily.

6) E. M. Burgess and C. L. Liotta, *J. Org. Chem.*, **46**, 1703 (1981); see also C. L. Liotta, *Tetrahedron Lett.*, **1975**, 519, 523.

7) In the Woodward-Hoffmann treatment, only the tilt of p-π-type orbitals are considered and the concomitant hybridization change is not handled formally.

8) P. Heimbach and R. Traunmuller, *Justus Liebigs Ann. Chem.*, **727**, 208 (1969).

9) J. Spanget-Larsen and R. Geisler, *Tetrahedron Lett.*, **23**, 2435 (1982); S. Ito and A. Kakehi, *Bull. Chem. Soc. Jpn.*, **55**, 1869 (1982).

10) The predominant π-MO extension of norbornene in the exo-direction has been rationalized also in terms of orbital mixing (S. Inagaki and K. Fukui, *Chem. Lett.*, **1974**, 509; S. Inagaki, H. Fujimoto, and K. Fukui, *J Am. Chem. Soc.*, **98**, 4054 (1976)).

11) R. Gleiter and J. Spanget-Larsen, *Tetrahedron Lett.*, **23**, 927 (1982).

12) In the symmetric approach of a proton, the 1s orbital of proton keeps its orthogonality to π^* and the symmetry of π is not broken with respect to the bisecting plane of ethylene molecule; thus, in this condition, the σ-π orbital mixing may be difficult to take place. An MO-calculation suggests that the asymmetric approach of proton is more advantageous to the new C-H bond formation than the symmetric approach (H. Fujimoto, N. Koga, M. Endo, and K. Fukui, *Tetrahedron Lett.*, **22**, 1263 (1981)).

13) According to W. L. Jorgensen and L. Salem (Ref. 3, p. 14), σ_{CC} levels lie generally higher than σ_{CH} ones in view of the magnitudes of CH and CC bond energies. Thus, the influence of the σ_{CH} (and the σ^*_{CH}) levels may be slight. The present treatment implies that these orbitals are regarded as orthogonal to others throughout the course of reaction.

14) W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2324 (1966).

15) Since MO-calculations are based on delocalized molecular orbitals, the energies of localized two-center orbitals cannot be obtained by calculation. Thus, in the present study, the energies of σ_{CC} and σ^*_{CC} in ethylene are approximated to the calculated values of $3A_g$ and $3A_u$ orbitals in which σ_{CC} and σ^*_{CC} are involved as an important fraction, respectively.: the localized σ_{CC} level should underlie the $3A_g$, and the counterpart σ^*_{CC} lie above the $3A_u$ level. The energies of $1B_{2u}$ and $1B_{3g}$, of course as they are, can be assigned to the π and π^*.

16) R. C. Weast, "Handbook of Chemistry and Physics," 66th ed. p. E-74, CRC Press, Boca Raton, Florida (1986).

17) Ref. 3, p. 10.

18) Since fraction r_1 in σ^*_{CC} or σ_{CC} is located closer to the 1s orbital than the counterpart fraction r_2 is, the phase relationship between fraction 1s (in ϕ_1 or ϕ_2) and fraction r_1 should be considered in preference to that between 1s and r_2.

19) Combinations $[\phi_3 - \sigma_{CC}]$ and $[\sigma^*_{CC} - \phi_1]$ should be assigned to the corresponding unoccupied levels.

20) Combinations $[\phi_3 + \sigma^*_{CC}]$ and $[\sigma^*_{CC} - \phi_3]$ should be assigned to the corresponding unoccupied levels.

21) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," Chap. 6, McGraw-Hill, Inc., New York (1969).

22) MO-calculations on methane and methyl bromide are available in the literature (methane: Ref. 14; methyl bromide: Y. Uehara, N. Saito, and T. Yonezawa, *Chem. Lett.*, **1973**, 495). Since the total valence electron energy of σ-system in a localized mode can be considered to be the same as that in a delocalized mode in principle, the energy of localized σ_{CH} (sp^3—1s) in methane may be given as the average value of three degenerated $1T_2$ levels and $2A_1$. Similarly, $2T_2$ and $3A_1$ levels give the corresponding σ^*_{CH} level. The σ_{CBr} and σ^*_{CBr} are approximated to $5A_1$ and $6A_1$ level of methyl bromide, in which the respective σ_{CBr} and σ^*_{CBr} fraction are involved predominantly: the localized σ_{CBr} level should underlie the $5A_1$ and the σ^*_{CBr} lie above the $6A_1$ level.

23) An MO-calculation on ethane is available: W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2201 (1967). Since localized MO's are dealt with here, the σ_{CC} and σ^*_{CC} should have not been perturbed by other levels. However, MO-caluculations give only delocalized levels; thus, in the present study, the σ_{CC} and σ^*_{CC} are approximated to the $3A_1$ and $3A_2$ levels of ethane, in which its σ_{CC} and σ^*_{CC} levels are involved as a predominant fraction, respectively. The localized σ_{CC} level should underlie the $3A_1$ and the σ^*_{CC} lie above the $3A_2$ level.

24) J. B. Peel and G. D. Willett, *Aust. J. Chem.*, **28**, 2357 (1975).

25) The HOMO level of *t*-BuOH should be the n orbital (2p) of hydroxy oxygen and may be assumed to have a near energy level to that of the n orbital located in *t*-BuO^-.

26) Since fraction 1s makes little contribution to ψ_2, the orbital amplitude of ψ_2 in 1-H is approximated to nil.

27) In the in-phase combination between ε_3 and σ^*_{CC}, fractions t_1 and u_2 and fractions t_2 and u_1 should be in an in-phase mode; because the basis t_1 and u_1 located in C^1 and the basis t_2 and u_2 located in C^2 are orthogonal, respectively.

28) The application of tilts of orbitals must be limited to the reactions or molecular deformations with relatively small geometrical change of nuclear configuration.

29) For a leading reference to the cis addition in norbornene, see T. G. Traylor, *Acc. Chem. Res.*, **2**, 152 (1969).

30) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2248 (1963). For a review of cis addition, see M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **3**, 245 (1964).

31) H. Kwart, T. Takeshita, and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2606 (1964).

32) Localized two-center MO's for ethyl bromide and ethylene generated can be obtained also by considering formally tilted σ_{CC}, σ^*_{CC}, π, and π^* in the starting ethylene molecule and formally tilted σ_{CC}, σ^*_{CC}, and combinations $[t_1 \pm t_2]$ in the ethyl bromide molecule, respectively.

33) J. P. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966). The computation was performed on an NEC PC-980IRX personal computer using the program composed by Professor Hisayoshi Kobayashi, Kyoto Prefectual University.