Geminal Bond Participation in the Sigmatropic [1,5]-Hydrogen Shifts: Relative Reactivities of *Z*- and *E*-1-Substituted 1,3-Pentadienes

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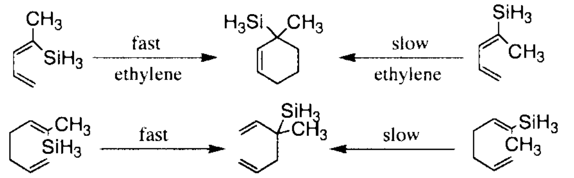
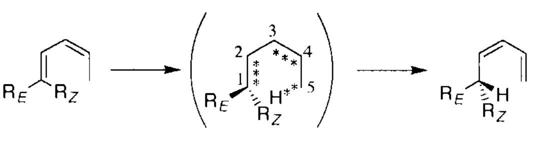
The analysis of the bond interactions at the transition states of the sigmatropic [1,5]-hydrogen shift of 1,3-pentadiene showed the significant participation of the σ bonds geminal to the reacting centers. The electron-donating σ bonds at the *Z*-positions in the 1-substituted 1,3-pentadienes were predicted to enhance the reactivities rather than those at the *E*-positions. The predictions of the relative reactivities of the *Z*- and *E*-isomers were confirmed by the calculated activation energies by the density functional theory calculations.

Recently, we disclosed the significant participation of σ bonds geminal to the reacting centers in the Diels–Alder reactions[1] and the Cope rearrangements.[2] Electron-donating σ bonds at the *Z*-positions in the terminal carbons of the dienes were found to enhance the reactivity more than those at the *E*-positions (Scheme 1). In this paper, we showed the geminal bond participation in the sigmatropic [1,5]-hydrogen shifts (eq 1), predicted the relative reactivities of *Z*- and *E*-1-substituted 1,3-pentadienes, and confirmed the prediction by the density functional theory calculations.

Scheme 1.





(1)

1, *E*: $R_Z = H, R_E = CH_3$; *Z*: $R_Z = CH_3, R_E = H$
2, *E*: $R_Z = H, R_E = NH_2$; *Z*: $R_Z = NH_2, R_E = H$
3, *E*: $R_Z = H, R_E = OH$; *Z*: $R_Z = OH, R_E = H$
4, *E*: $R_Z = CH_3, R_E = SiH_3$; *Z*: $R_Z = SiH_3, R_E = CH_3$
5, *E*: $R_Z = NH_2, R_E = PH_2$; *Z*: $R_Z = PH_2, R_E = NH_2$
6, *E*: $R_Z = OH, R_E = SH$; *Z*: $R_Z = SH, R_E = OH$

The electron delocalization from the σ bonds geminal to a reacting π bond to another reacting bond is generally different from the delocalization to the geminal σ bonds in the phase relation of the orbitals involved (Figure 1). When electrons delocalize from the geminal σ bonds to an electron accepting bond (A), the cyclic orbital interaction among the two σ bonding orbitals and the accepting orbital (a*) occurs as shown in Figure 1a. The cyclic orbital interactions are under the control of the orbital phase continuity–discontinuity properties.[3] The phase continuity requires that the σ and a* orbitals are in phase while the σ orbitals are out of phase. The cyclic interaction cannot simultaneously satisfy these requirements. This suggests that stronger σ→a* delocalization is bonding but the other is antibonding. When the delocalization from a donating bond (D) to the geminal σ bonds, the cyclic interaction also occurs among the σ* antibonding orbitals of the geminal bonds and the donating orbital (d). The phase continuity requires that the d, σ* and σ* orbitals are in phase with one another (Figure 1b).[3] The cyclic interaction satisfies these requirements. Both d→σ* delocalizations should effectively occur in bonding manner. The delocalizations from the geminal bonds have the bonding-antibonding properties opposite to each other, while the delocalizations to the geminal bonds are both bonding. Consequently, the delocalization from the geminal σ bonds should play crucial roles in the geminal bond participation rather than that to the geminal σ bonds. In fact, this was previously confirmed in the geminal bond participation in the Diels–Alder reactions[1] and the Cope rearrangements.[2]

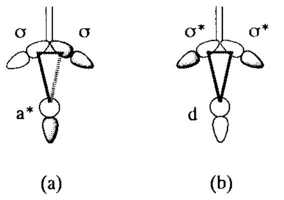


Figure 1. Orbital phase properties in the cyclic interactions of the geminal σ bonds with an electron-accepting (A) and donating σ bonds (D). (a) the discontinuity in the σ–σ–a* interaction; (b) the continuity in the σ*–σ*–d interaction.

We investigated the bond interactions at the transition state of the suprafacial process of the [1,5]-hydrogen shift of 1,3-pentadiene by applying the bond model method.[1,4] The interaction between the bond orbitals, *i* and *j*, was estimated by the interbond energy (IBE) and interbond population (IBP) defined as below:[6]

$$\mathrm{IBE}(i,j) = P_{ij}(H_{ij}+F_{ij}) \qquad (2)$$

$$\mathrm{IBP}(i,j) = 2P_{ij}S_{ij} \qquad (3)$$

where P_{ij}, F_{ij}, H_{ij} and S_{ij} are the elements of the density, Fock, core Hamiltonian and overlap matrixes, respectively. The calculated IBE and IBP values are listed in Table 1. The electron delocalization from the π_{C1-C2} orbital to the breaking σ^*_{C5-H} orbital most stabilizes the transition state (IBE = –1.2989, IBP = 0.2094). The stabilization due to the delocalization from the breaking σ_{C5-H} orbital to the π^*_{C3-C4} orbital and that from the π_{C3-C4} orbital to the π^*_{C1-C2} orbital are also remarkable (IBE = –0.7132 and –0.9002 au, respectively). The stabilization is greater than that due to the reverse delocalizations [$\mathrm{IBE}(\sigma_{C5-H}\rightarrow\pi^*_{C1-C2}) = -0.4886$ au, $\mathrm{IBE}(\pi_{C1-C2}\rightarrow\pi^*_{C3-C4}) = -0.3713$ au, $\mathrm{IBE}(\pi_{C3-C4}\rightarrow\sigma^*_{C5-H}) = -0.1921$ au].

A remarkable difference was found in the delocalization from the σ_{C-H} bonds geminal to the reacting terminal π bond to the breaking σ_{C5-H} bond (Table 1 and Figure 2). The signs of the IBE and IBP values showed the opposite bonding-antibonding

Table 1. Interbond energies (au) and interbond populations at the transition state of the sigmatropic [1,5]-hydrogen shift of 1,3-pentadiene

Interactions	IBE	IBP
$\pi_{C1-C2} - \sigma^*_{C5-H}$	–1.2989	0.2094
$\sigma_{C5-H} - \pi^*_{C1-C2}$	–0.4886	0.0807
$\sigma_{C5-H} - \pi^*_{C3-C4}$	–0.7132	0.1190
$\pi_{C3-C4} - \sigma^*_{C5-H}$	–0.1921	0.0331
$\pi_{C3-C4} - \pi^*_{C1-C2}$	–0.9002	0.1485
$\pi_{C1-C2} - \pi^*_{C3-C4}$	–0.3713	0.0628
$\sigma_{C1-HZ} - \sigma^*_{C5-H}$	–0.0139	0.0022
$\sigma_{C1-HE} - \sigma^*_{C5-H}$	0.0600	–0.0104
$\sigma_{C5-H} - \sigma^*_{C1-HZ}$	–0.0350	0.0047
$\sigma_{C5-H} - \sigma^*_{C1-HE}$	–0.0698	0.0103

properties of the delocalization from the geminal C1–H_Z and C1–H_E bonds as was predicted. The delocalization from the σ_{C1-HZ} orbital to the breaking σ^*_{C5-H} orbital is bonding (IBE = –0.0139, IBP = 0.0022) while that from the σ_{C1-HE} orbital (0.0600, –0.0104) is antibonding. The reverse delocalizations to the geminal C1–H_Z and C1–H_E bonds are both bonding. The delocalization (IBE = –0.0698, IBP = 0.0103) to the σ^*_{C1-HE} orbital stabilizes the transition state more than that (IBE = –0.0350, IBP = 0.0047) to the σ^*_{C1-HZ} orbital.

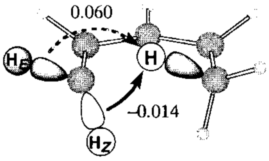


Figure 2. Geminal bond participation of the [1,5]-sigmatropic hydrogen shift of 1,3-pentadiene. The values are the interbond energies (au). The minus sign indicates the bonding interactions (*vice versa*).

The analysis of the bond interactions suggested that the reactions are accelerated when the σ_{C-HZ} is electron-donating bond or the σ_{C-HE} is electron-accepting bond. The geminal bond participation led to the prediction that the 1-substituted 1,3-pentadienes with electropositive atom substituents at the *Z*-positions should be more reactive than those at the *E*-positions. The high σ bonding orbital energy promotes the bonding delocalization from the σ bond to the breaking σ_{C-H} bond. Electronegative atom substituents at the *E*-positions lower the σ bonding orbital energy to decrease the antibonding delocalization from the σ bond to the breaking σ_{C-H} bond.

We calculated the relative reactivities of *Z*- and *E*-1-substituted 1,3-pentadienes in order to confirm the prediction.[4] The *E*-isomers of the dienes **1**–**3** substituted by the methyl, amino, and hydroxy groups have a relatively electropositive C–H bond at the *Z*-position and then were predicted to be more reactive than the *Z*-isomers. This was in agreement with the calculated activation energies of the reactions (Table 2). The small $\delta\Delta E^{\ddagger}$ value in **3** relative to **2** should be attributed to the decreased donating ability of the C–H bond due to the inductive effect of the hydroxy oxygen. In fact, the σ_{C-H} orbital energy in vinyl alcohol is lower than that in vinyl amine (–0.741 au and –0.722 au, respectively). Moreover, we compared the relative reactivities of the *Z*- and *E*-isomers **4**–**6** with the substituent atoms in the same group of the periodic table. The second-row element substituents at the *Z*-position were predicted to enhance the reactivity rather than those at the *E*-position. The predictions were confirmed by the calculated relatively low activation energies of the *Z*-isomers. The small $\delta\Delta E^{\ddagger}$ value in **6** is due to the donating ability of the C–S bond lowered by the inductive effect of the hydroxy oxygen.

Table 2. Activation energies[a] (kcal/mol) of the sigmatropic [1,5]-hydrogen shifts of *Z*- and *E*-1-substituted 1,3-pentadienes and energy differences[a] (kcal/mol) between the *Z*- and *E*-isomers in the reactants and the transition states

Dienes	$\Delta E_E^{\ddagger}$ [b]	$\Delta E_Z^{\ddagger}$ [b]	$\delta\Delta E^{\ddagger}$ [c]	ΔE_R [d]	ΔE_{TS} [d]
1	38.9	40.6	1.7	1.73	3.44
2	40.1	43.8	3.7	1.12	4.83
3	38.9	42.2	3.3	0.64	3.91
4	42.7	40.0	–2.7	0.34	–2.36
5	44.9	42.0	–2.9	0.78	–2.12
6	41.8	41.0	–0.8	0.72	–0.10

[a] B3LYP/6–31G* energies including zero-point energies. [b] Activation energies based on the most stable rotatomer. [c] $\delta\Delta E^{\ddagger} = \Delta E_Z^{\ddagger} - \Delta E_E^{\ddagger}$. [d] Energy differences in the reactants, ΔE_R, and those in the transition states, ΔE_{TS}. $\Delta E = E(Z\text{-isomer}) - E(E\text{-isomer})$.

The energy differences in the transition states, ΔE_{TS}, in most of the reactions are greater than those in the reactants, ΔE_R (Table 2). This supported that the reactivities are controlled by the stabilization of the transition state rather than the relaxation of the steric repulsion in the *Z*-isomers of the reactants.

The geminal bond participation controls the relative reactivities of the *Z*- and *E*-1-substituted 1,3-pentadienes in the sigmatropic [1,5]-hydrogen shifts.

References and Notes

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3 a) The orbital phase continuity requirements[3b] for the effective cyclic orbital interactions are as follows: electron donating orbitals are out of phase; electron accepting orbitals are in phase; donating and accepting orbitals are in phase. The cyclic interaction that simultaneously satisfies the three requirements promotes the electron delocalization. Otherwise, the electron delocalization cannot effectively occur. b) K. Fukui and S. Inagaki, *J. Am. Chem. Soc.*, **97**, 4445 (1975).
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7 a) Mulzer and his colleagues[7b] recently proposed that the stereoselectivities in the sigmatropic [1,5]-hydrogen shifts are controlled by the steric effects at the transition states. b) C. Dehnhard, M. McDonald, S. Lee, H. G. Floss, and J. Mulzer, *J. Am. Chem. Soc.*, **121**, 10848 (1999).