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Thermal Ring-Splitting Reactions of Diarylcyclobutanes: Significance of Steric Effects on Orbital Interactions in Transition States and Biradical Intermediates

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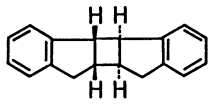
Regiochemistry and reactivities in the thermal ring-splitting reactions of diarylcyclobutanes (**1**—**5**) have been studied and shown to depend on the stable conformations and rotational mobilities of the aryl substituents. The reactions of **1** and **2** result in a regiospecific symmetric cleavage to give indene or styrene along with significant isomerization of **2** to **3**. In the cases of **3**—**5** both the symmetric and unsymmetric cleavages competitively occur with decreasing symmetric-to-unsymmetric ratios with an increase in methyl substitution. The olefin products from **4** are mixtures of *cis*- and *trans*-2-butene, *cis*- and *trans*-β-methylstyrene, and *trans*-stilbene. Thermochemical analyses combined with product analyses indicate that the symmetric cleavage of **1** and the unsymmetric cleavage of **3** proceed with a concerted mechanism, whereas 1,4-biradicals are involved in the other reactions. Structure-reactivity relationships of the present reactions are discussed in terms of mixing of the σ* character in a bonding MO by specific π-σ* interactions, depending on the conformational situations of the aryl groups and in terms of the steric effects which destabilize 1,4-biradicals as well as transition states of the biradical fragmentation to the olefins.

Ring-splitting reactions of cyclobutanes have beeen providing an excelent diagnosis method for exploring the steric and electronic factors controlling chemical reaction courses.[1-3] Theories predict that concerted [$_\sigma 2_s + _\sigma 2_s$] cycloreversions are forbidden in the ground state.[4] A considerable body of stereochemical and thermochemical evidence indeed supports mechanisms involving 1,4-biradicals in thermal ring-splitting and stereomutation reactions of cyclobutanes with no particular π substituents such as parent cyclobutane,[5,6] alkylcyclobutanes,[7] divinylcyclobutane,[8] and other substituted cyclobutanes,[9] as shown by molecular-orbital considerations.[10,11]

On the other hand, much less has been investigated concerning mechanistic details of thermal reactions of cyclobutanes with large π substituents. It can be presumed that the chemical behavior must be remarkably susceptible to steric and electronic effects of such π substituents, since the cyclobutane rings are small in size and conformationally rigid[12] and since the π-bonding character contributes to the ring σ framework.[13] Since vibrational motions of a C-C bond with a large substituent are very slow, the rate-determining step for the ring cleavage of such cyclobutanes may be not scisson of a C-C bond but rotation or other motions.

It was reported that thermolyses of substituted tetrahydrocyclobuta[*a*]naphthalenes[14] and [4.4.2]propelladienes[15] result in regiospecific ring cleavages to give aromatized products and olefin fragments with high stereoretention. Although the high stereoselectivities would be attributable to steric inhibition of bond rotaion in 1,4-biradicals, an attractive alternative is the participation of a concerted mechanism that would occur as the consequence of extended π conjugation in transition states. This was suggested for thermal reactions of phenylated oxetanes[16] and *cis*-3,6-diphenyl-1,2-diazacyclohexene.[17] Of another stereochemical interest in bond cleavages of π-substituted cyclobutanes are regioselectivities, which would reflect the relative stabilities of different biradicals or which would be controlled by interactions of the π orbitals with each of the σ orbitals of the cyclobutane ring along the reaction coordinate.[1,18]

From the above points of view, we have investigated thermal ring-splitting reactions of diarylcyclobutane (**1**—**5**). It can be expected that the stereochemical features and reactivities of the reactions are controlled by complex combinations of steric and electronic effects of the aryl substituents. We report here mechanistic details concerning the ring-splitting reactions and the significance of steric control of orbital interactions in the stereochemical reaction courses.



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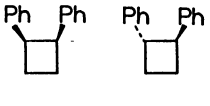

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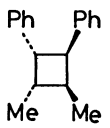

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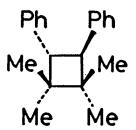

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Experimental

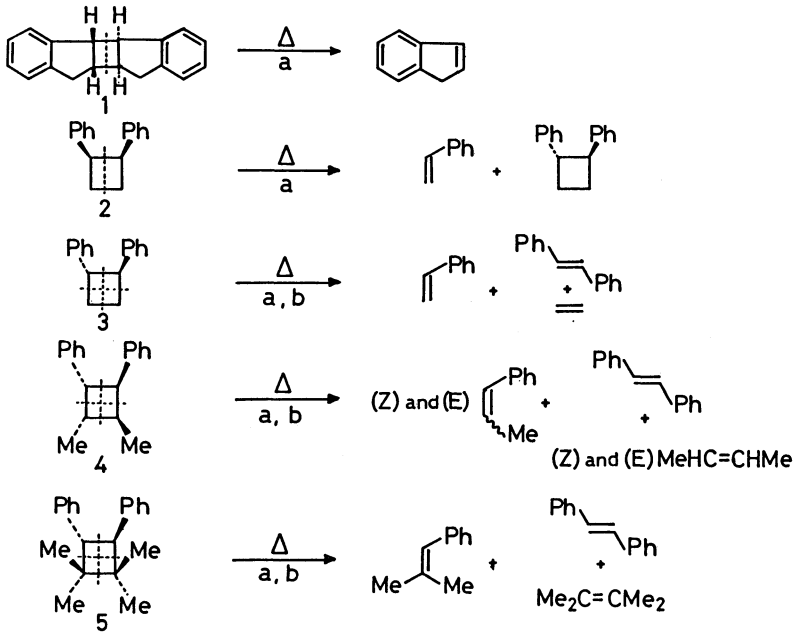
The cyclobutanes were prepared according to methods described in the literature; *cis-transoid-cis*-cyclobuta[1,2-*a*; 4,3-*a'*]diindene (**1**),[19] *cis*-1,2-diphenylcyclobutane (**2**),[20] *trans*-1,2-diphenylcyclobutane (**3**),[20] *r*-1, *t*-2-dimethyl-*t*-3, *c*-4-diphenylcyclobutane (**4**),[18b] and 1,1,2,2-tetramethyl-*trans*-3,4-diphenylcyclobutane (**5**).[21] Purification was carried out by repeated recrystallization from methanol for **1** and **2** or from hexane for **5**, whereas **3** and **4** were distilled in vacuo. Diphenyl ether was used after vacuum distillation.

Aliquot portions (2 cm^3) of a diphenyl ether solution of **1**—**5** (0.02 mol dm^{-3}) were introduced into Pyrex tubes (8 mm i.d.), thoroughly degassed by three freeze-pump-thaw cycles under $<10^{-3}$ Torr, and then heated in a Shimadzu GC-6AM electric furnace that had been preheated at given temperatures (±<1 °C). The reactions were followed by vapor-phase chromatography on a Shimadzu GC-8A machine using a 3-m column of 5% OV-17 on Chromosorb W AW-DMCS.

Results

Thermal reactions of **1**—**5** were performed by heating a degassed diphenyl ether solution (0.02 mol dm^{-3}) at 160—360 °C. The products were exclusively the corresponding olefins, except for the case of **2** where the isomerization to **3** significantly occurred, as shown in Scheme 1. In the cases of **1** and **2**, the ring cleavage is regiospecific in the symmetric (*a*) direction, whereas **3**—**5** are cleaved in both the symmetric (*a*) and the unsymmetric (*b*) directions in *a*:*b* ratios decreasing with an increase in methyl substitution. Although the formation of ethylene, 2-butene, and 2,3-dimethyl-2-butene was confirmed, their yields were not determined because of analytical difficulties. However the yields of the other products accounted for the conversions of the cyclobutanes within experimental errors (≤5%). It was confirmed that no isomerization of **3** to **2** occurs at all. Similarly, the stereomutation of **4** should be negligible, if any, since no product other than the olefins was detected at all by vapor-phase chromatography (VPC), and since the combined yields of β-methylstyrene and stilbene virtually equaled the amounts of **4** consumed. Although the stilbene formed from **3**—**5** was only the trans isomer, **4** gave a mixture of *cis*- and *trans*-2-butene in a ca. 35 : 65 ratio independently of temperature and mixtures of *cis*- and *trans*-β-methylstyrene in ratios increasing with an increase in the temperature from 15 : 85 at 280 °C to 27 : 73 at 320 °C. It was confirmed that each isomer of either stilbene or β-methylstyrene is not isomerized at ≤360 °C.

The total rate constants (k_t) for the thermal reactions at various temperature were determined from linear plots of $\ln(C/C_0)$ vs. the reaction time in seconds; C_0 and C represent the concentrations of each cyclobutane before thermolysis and at a given reaction time, respectively. Although k_t equals the rate constant (k_a) for the symmetric cleavage of **1**, each rate constant (k_a, k_b, or k_i) for the symmetric or the unsymmetric cleavage of **2**—**5** or for the isomerization of **2** to **3** at a given temperature was obtained from k_t multiplied by the molar proportion of the relevant product, styrene product/(styrene product+2×stilbene or 2×**3**), 2×stilbene/(styrene product+2×stilbene), or 2×**3**/(styrene+2×**3**). Table 1 summarizes the calculated rate constants at various temperatures. Figure 1 shows Arrhenius plots of ln k_a, ln k_b, and ln k_i vs. T^{-1} from which the activation enthalpies ($\Delta H_a^{\neq}$, $\Delta H_b^{\neq}$, and $\Delta H_i^{\neq}$) and the frequency factors (A_a, A_b, and A_i) were obtained, as listed in Table 2. In the case of **5**, the unusually high activation barriers and frequency factors appear to involve large experimental errors, because of the very slow reaction occurring even at very high temperatures. Nevertheless, the observed values should indicate that the thermochemical parameters are much larger than those of the other cyclobutanes, thus being of mechanistic significance. Figure 2 shows a plot of ln (cis-trans ratio) vs. T^{-1} for the β-methylstyrene formation from **4**, which gives an activation enthalpy difference of 44.3 kJ mol^{-1}



Scheme 1.

Table 1. Rate Constants for Thermal Reactions of **1**—**5**[a)]

1	T/K	493	503	513	523		
	$k_t=k_a$/s^{-1}	1.46×10^{-5}	4.27×10^{-5}	8.73×10^{-5}	1.41×10^{-4}		
2	T/K	433	443	453	463	473	
	k_t/s^{-1}	8.63×10^{-7}	2.65×10^{-6}	6.45×10^{-6}	1.87×10^{-5}	4.44×10^{-5}	
	k_a/s^{-1}	6.13×10^{-7}	1.98×10^{-6}	4.98×10^{-6}	1.43×10^{-5}	3.42×10^{-5}	
	k_i/s^{-1}	2.50×10^{-7}	6.77×10^{-7}	1.47×10^{-6}	4.36×10^{-6}	1.02×10^{-5}	
3	T/K	493	503	513	523		
	k_t/s^{-1}	2.37×10^{-5}	5.83×10^{-5}	1.10×10^{-4}	2.55×10^{-4}		
	k_a/s^{-1}	2.27×10^{-5}	5.64×10^{-5}	1.06×10^{-4}	2.47×10^{-4}		
	k_b/s^{-1}	9.67×10^{-7}	1.88×10^{-6}	4.04×10^{-6}	7.48×10^{-6}		
4	T/K	553	558	563	568	573	578
	k_t/s^{-1}	4.60×10^{-6}	6.13×10^{-6}	9.44×10^{-6}	1.52×10^{-5}	2.32×10^{-5}	3.20×10^{-5}
	k_a/s^{-1}	3.40×10^{-6}	4.39×10^{-6}	6.75×10^{-6}	1.16×10^{-5}	1.68×10^{-5}	2.39×10^{-5}
	k_b/s^{-1}	1.20×10^{-6}	1.74×10^{-6}	2.70×10^{-6}	3.57×10^{-6}	6.37×10^{-6}	8.10×10^{-6}
	T/K	583	588	593	598	603	
	k_t/s^{-1}	4.56×10^{-5}	5.71×10^{-5}	8.55×10^{-5}	1.63×10^{-4}	2.42×10^{-4}	
	k_a/s^{-1}	3.47×10^{-5}	4.22×10^{-5}	6.25×10^{-5}	1.24×10^{-4}	1.88×10^{-4}	
	k_b/s^{-1}	1.10×10^{-5}	1.49×10^{-5}	2.31×10^{-5}	3.88×10^{-5}	5.38×10^{-5}	
5	T/K	603	613	623	633		
	k_t/s^{-1}	3.14×10^{-6}	1.11×10^{-5}	2.78×10^{-5}	6.15×10^{-5}		
	k_a/s^{-1}	4.36×10^{-7}	1.58×10^{-6}	3.95×10^{-6}	9.05×10^{-6}		
	k_b/s^{-1}	2.70×10^{-6}	9.47×10^{-6}	2.38×10^{-5}	5.24×10^{-5}		

a) k_t, rate constant for the consumption of **1**—**5**; k_a, rate constant for the symmetric cleavage of **1**—**5**; k_b, rate constant for unsymmetric cleavage of **3**—**5**; k_i, rate constant for the isomerization of **2** to **3**.

Table 2. Thermochemical Parameters for Thermal Reactions of **1**—**5**[a)]

	1	**2**		**3**		**4**		**5**	
	a	a	i	a	b	a	b	a	b
$\Delta H^{\neq}$/kJ mol^{-1}	161.5	167.4	161.1	166.5	148.1	218.8	208.4	308.4	304.2
$\log A$	12.4	14.0	12.8	13.0	9.7	15.2	13.7	20.6	21.0
$\Delta S^{\neq b)}$/e.u.	−3.8	+3.5	−2.0	−1.1	−16.2	+9.0	+2.2	+37.0	+37.9

a) The letters a, b, and i refer the symmetric ring cleavage, the unsymmetric one, and the isomerization of **2** to **3**. b) Values at 300 K obtained by assuming that the transmission coefficient (κ) is unity.

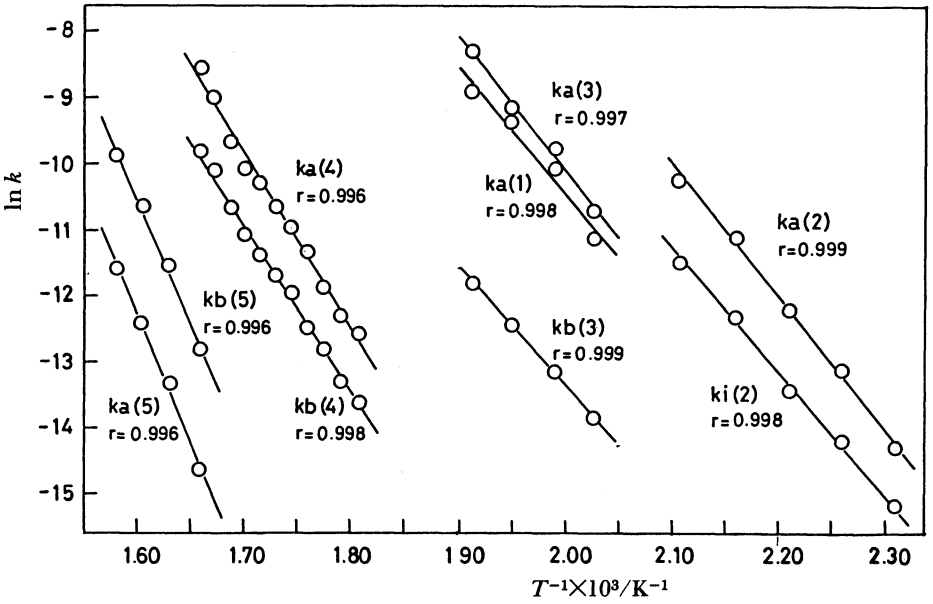


Fig. 1. Arrhenius plots for the thermal reactions of **1**—**5**. k_a, k_b, and k_i are the rate constants for the symmetric cleavage, the unsymmetric cleavage, and the isomerization of **2** to **3**, respectively. Data are from Table 1.

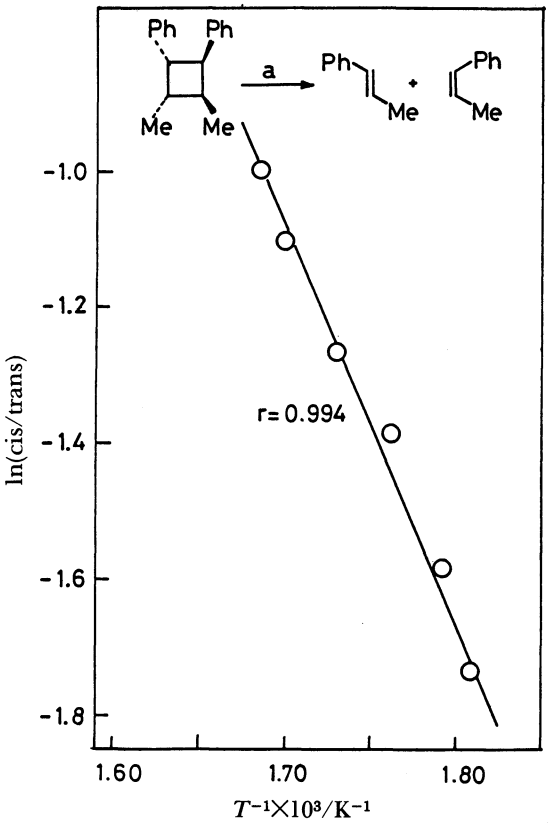


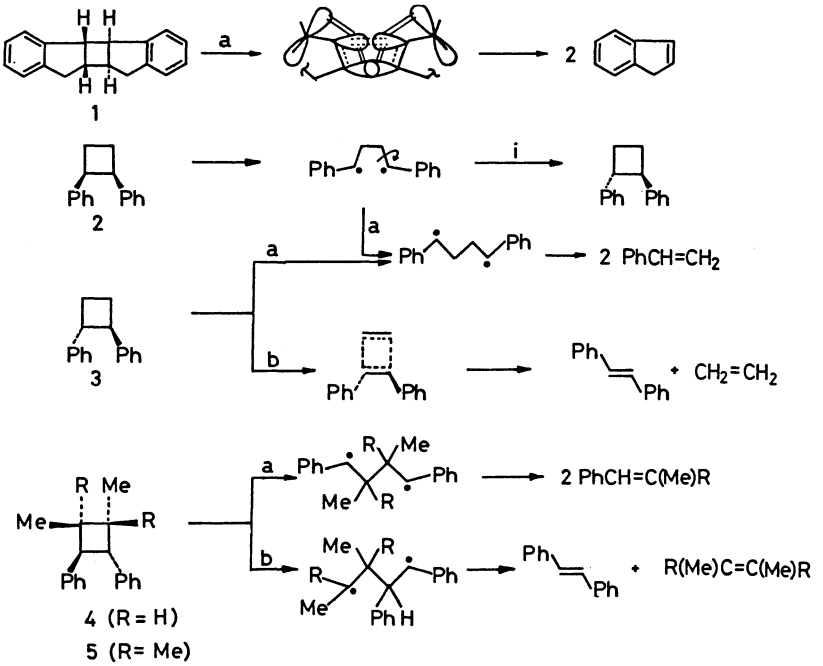
Fig. 2. Plot of ln(cis-trans ratio of β-methylstyrene) vs. T^{-1} for the symmetric cleavage of **4**

and log (A_{cis}/A_{trans}) of 3.4.

Discussion

Mechanisms. The significant isomerization of **2** to **3** and the losses of stereointegrity in the olefin formation from **4** strongly suggest the intervention of 1,4-biradicals in these reactions. The activation barriers for the symmetric cleavage of **1**—**3** are lower by 94—96 kJ mol^{-1} than that of parent cyclobutane.[6] The differences are similar to the energy gained by the benzylic stabilization of 1,4-butanediyl, 2×54 kJ mol^{-1}. Similarly, $\Delta H_b^{\neq}$ of **4** is a value which is expected for a biradical mechanism for unsymmetric cleavage. Furthermore, the frequency factor for the symmetric cleavage of **3** is very similar to those for the isomerization of *trans*-1,2-divinylcyclobutane which proceeds by way of 1,4-biradicals.[8] The high activation barriers and the large frequency factors for the symmetric cleavage of **4** and, in particular, for both the symmetric and the unsymmetric cleavages of **5** are not accommodated with a concerted mechanism, but with considerable structure changes from the relatively rigid cyclobutanes to very loose transition states.

It is of mechanistic significance to note that log A_a of **1** is unusually low for such a two-bond splitting reaction by way of a discrete 1,4-biradical from a very rigid molecule. Since the transition state should be very tight, as shown by the negative entropy change, the symmetric cleavage of **1** appears to proceed by a concerted or concerted-like mechanism. The rigid tricyclic structure is certainly favorable for efficient orbital overlap between the C-C bonds being broken with minimum molecular motions. By the same token, the unsymmetric cleavage of **3** should be concerted since $\Delta S_b^{\neq}$ at 300 K is −16.2 e.u., still more negative than the entropy change for the concerted Cope rearrangement of *cis*-1,2-divinylcyclobutane to 1,5-cyclooctadiene.[8] Futhermore, $\Delta H_b^{\neq}$ of **3** is much smaller than that of **4** and even smaller than a calculated enthalpy difference (≈163 kJ mol^{-1}) between **3**



Scheme 2.

and 1,2-diphenyl-1,4-butanediyl.[2,23] Effective vibrational motions are probably not inhibited by any steric interactions in **3**, thus realizing the simultaneous cleavage of the C1-C4 and C2-C3 bonds. Scheme 2 summarizes the mechanisms for the thermal reactions of **1**—**5**.

Stereoelectronic Effects on Regioselectivities and Reactivities. The present thermal reactions can not be interpreted in terms of simple steric and electronic effects, e.g., steric assistance of bond breaking by nonbonding interactions between the substituents or benzylic stabilization of 1,4-biradicals. For instance, $\Delta H_a^{\neq}$ of **4** is higher than $\Delta H_b^{\neq}$, even though the 1,4-biradical intermediate for the symmetric cleavage is evidently more stable than that for the unsymmetric one. Another interesting observation is that $\Delta H_a^{\neq}$ of **2** is almost identical with that of **3** irrespective of large steric repulsion between the cis phenyl groups expected for **2**. It appears that both the regioselectivities and the reactivities are controlled by restricted conformations and torsional mobilities of the aryl substituents associated with specific orbital interactions, as demonstrated for photochemical reactions of the cyclobutanes.[1,18]

Figure 3 shows different stable conformations of the aryl substituents, case (i) and case (ii), with respect to each of the ring C-C bonds; the arylated carbon atoms

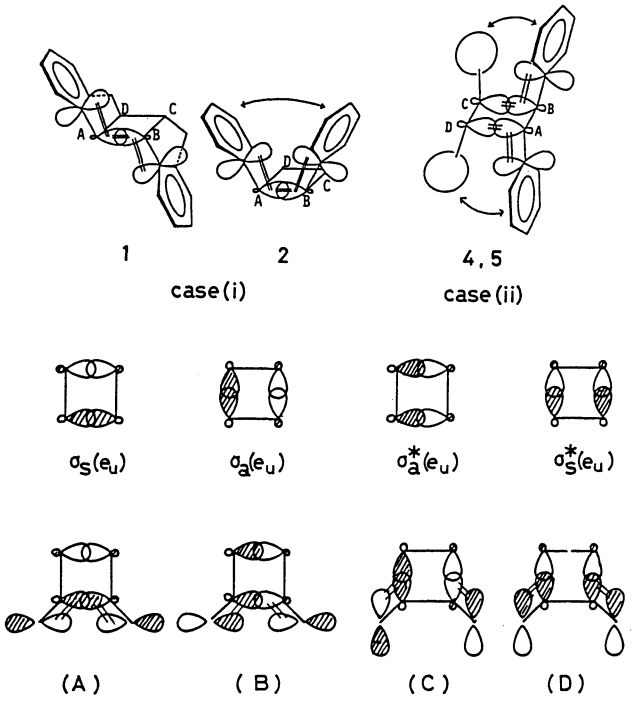


Fig. 3. Top: Different situations for stable rotameric conformations of the aryl rings, case (i) for **1** and **2** and case (ii) for **4** and **5**, associated with specific orbital interactions. Middle: Salem's σ and σ^* orbitals relevant for interactions with the π combinations. Bottom: (A) π_s-σ_s and (B) π_a-σ_a^* interactions occurring in case (i) and (C) π_a-σ_a and (D) π_s-σ_s^* interactions in case (ii)

are abbreviated as C_A and C_B and the others as C_C and C_D for convenience. In order to elucidate implications of orbital interactions in the present reactions, we consider conformation-controlled interactions of Salem's σ and σ^* orbitals of the cyclobutane ring[24] with combinations of the π orbitals, $\pi_s=\pi_A+\pi_B$ and $\pi_a=\pi_A-\pi_B$; subscript s or a denotes the symmetric or antisymmetric character with respect to two-fold rotation or reflection. In case (i), π_s-σ_s (A in Fig. 3) and π_a-σ_a^* (B) interactions can occur to give the highest occupied MO, $\pi_s-\lambda_1\sigma_s$ and a lower bonding MO, $\pi_a+\lambda_1^*\sigma_a^*$, respectively.[25] Similarly, π_a-σ_a (C) and π_s-σ_s^* (D) interactions may occur in case (ii) to give the bonding MO's, $\pi_a-\lambda_2\sigma_a$ and $\pi_s+\lambda_2^*\sigma_s^*$. The π-σ^* interactions should result in mixing of the σ_a^* or σ_s^* character to bring about a weakening of the relevant C-C bonds of the cyclobutane ring, while such bond-weakening effects can not be expected for the π-σ interactions. It is, therefore, reasonable to presume that the π_a-σ_a^* and π_s-σ_s^* interactions are responsible for the symmetric and the unsymmetric cleavages respectively.

It was reported that significant mixing of σ^* character in a bonding MO occurs by through-bond coupling between two π orbitals separated by a C-C bond to bring about unusual elongation of this bond.[26,27] Although the cyclobutane-ring C-C bonds of **1**, **2**, and **5** are not particularly long in common,[28] extensive vibrational and puckering motions of the cyclobutane ring might perturb the σ^* orbitals to allow significant π-σ^* interactions. It should be noted that the π_a-σ_a^* interactions are inherently more effective to through-bond coupling between π_A and π_B than the π_s-σ_s^* interactions. It can, therefore, be predicted that the symmetric cleavage selectively occurs unless there is particular steric inhibition in the orbital interactions. On the other hand, the unsymmetric cleavage may compete with the symmetric one in cases where π_a-σ_a^* interactions are sterically inhibited. This prediction is in good accord with the observed regioselectivities in the reactions of **1**—**5**.

On the basis of these arguments, the reason why $\Delta H_a^{\neq}$ of **3** is almost identical with that of more congested **2** can be easily interpreted by assuming that π_a-σ_a^* interactions are essential in the transition state of the symmetric cleavage of **2** and **3**. Furthermore, the lower-frequency factor for the symmetric cleavage of **3** than that of **2** indicates that a net loss of the rotational motions of the phenyl groups is required for the π_a-σ_a^* interactions in the transition state of **3**, while the orbital interactions are realized with least rotational motions in the case of **2**. Similarly, the thermochemical parameters reveal that the unsymmetric cleavage of **4** proceeds without either significant steric hindrance or large structure changes, being accommodated with the process from stable case (ii) conformations to the π_s-σ_s^* transition state. On the other hand, the relatively large values of $\Delta H_a^{\neq}$ and $\log A_a$ for

the symmetric cleavage of **4** are attributable to steric inhibition of case (i) conformations required for the π_a-σ_a* in transition state. In the case of **5**, the very high activation barriers and the unusually large frequency factors are certainly accommodated with very loose transition states, thus suggesting that the rate-determining step is no longer the orbital interactions but, perhaps, bond breaking of 1,4-biradicals.

Steric Effects on Reactivities of 1,4-Biradicals. Activation enthalpies for cyclization and fragmentation of 1,4-biradicals are usually ca. 30 kJ mol^{-1} in the absence of particular steric inhibition.[2] The cyclization of 1,4-diphenylbutanediyl must suffer a remarkable steric hindrance by the phenyl substituents at the radical centers to require a high activation barrier. Calculations according to the additivity of bond and group properties[2,23] allow us to estimate the heat of formation of **3** or 1,4-diphenylbutanediyl (**3**-BR$_a$) which is 245.8 kJ mol^{-1} or 353.6 kJ mol^{-1} each. The activation enthalpy for the cyclization of **3**-BR$_a$ is, therefore, calculated from the estimated values of the heat of formation and $\Delta H_a^{\neq}$ to be ca. 58 kJ mol^{-1}, a relatively large value in accord with the prediction of remarkable steric hindrance. Moreover, the relatively low value of log A_i of **2** is comparable to that for the isomerization of *cis*-1,2-diphenylcyclopropane.[22] Consequently, the significant isomerization of **2** to **3** is not attributable to the cyclization of a thermally equilibrated 1,4-biradical but, rather, to torsion about PhC-C of a non-streched 1,4-biradical followed by efficient bonding with least motion. On the other hand, the biradical fragmentation of **2** or **3** to styrene appears to proceed with a lower activation barrier since an orbital overlap between each of the radical centers and the C$_C$-C$_D$ bond is easily achieved without steric inhibition.

In the cases of **4** and **5**, however, steric hindrance should be significant for both the ring closure and the fragmentation of 1,4-biradicals because of the substitution of the methyl or the phenyl group at each carbon, as shown in Fig. 4. Extensive gauche interactions in the biradical (**4**-BR$_a$) for the symmetric cleavage of **4** certainly destabilize the biradical to contribute, at least in part, to the high value of $\Delta H_a^{\neq}$, while such steric interactions are less in **4**-BR$_b$, the biradical for the unsymmetric cleavage. Provided that the biradical fragmentation requires orbital overlap between each of the radical centers and the C-C bond being broken,[2,29] the transition state for the *cis*-β-methylstyrene from **4**-BR$_a$ should require much greater vibrational motions than that for the trans-olefin formation. This is in line with the observed difference in either the activation enthalpy or the frequency factor for the formation of *cis*- and *trans*-β-methylstyrene. The rotation of the massive PhCH group is perhaps rate determining. On the other hand, the temperature-independent cis-trans ratio in the 2-butene formation from **4** implies that the rate-determining step is the initial cleavage of C$_A$-C$_D$ (C$_B$-C$_C$) of the cyclobutane ring, since the rotation of the light MeCH group of **4**-BR$_b$ should be very rapid.

In particular, the biradicals of **5** (**5**-BR$_a$ and **5**-BR$_b$) are clearly very crowded and perhaps destabilized by large nonbonding interactions between the substituents.[30] The radical centers of **5**-BR$_a$ suffer large steric repulsion with the bulky substituents at quarter-

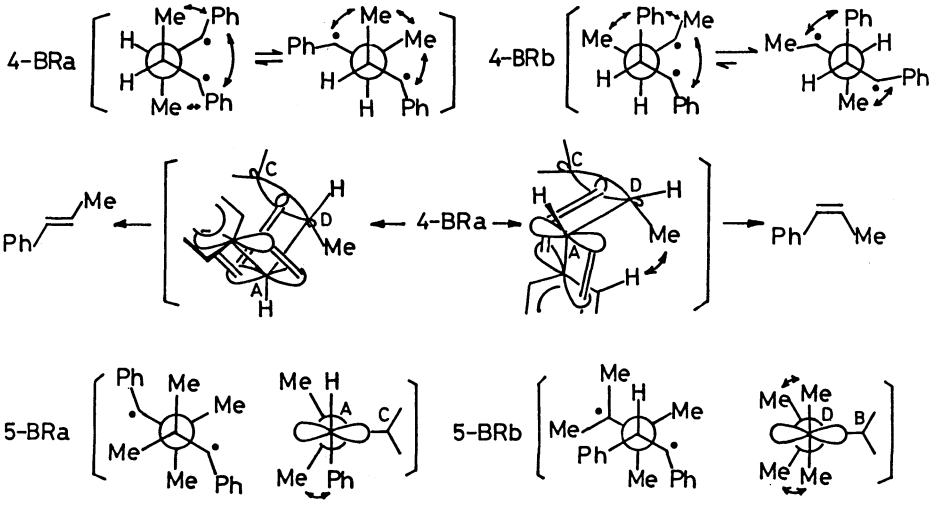


Fig. 4. Top: Newman projection formulas of **4**-BR$_a$ and **4**-BR$_b$ showing that the former is sterically more crowded than the latter. Middle: Perspective illustration of hypothetical transition states for the biradical fragmentation of **4**-BR$_a$ to *cis*- and *trans*-β-methylstyrene. Bottom: Newman projection formulas of **5**-BR$_a$ and **5**-BR$_b$ showing that either of the biradicals is sterically very crowded and that the radical centers are sterically hindered either in taking a planar conformation or in overlapping between the p orbitals and the C-C σ orbitals being broken.

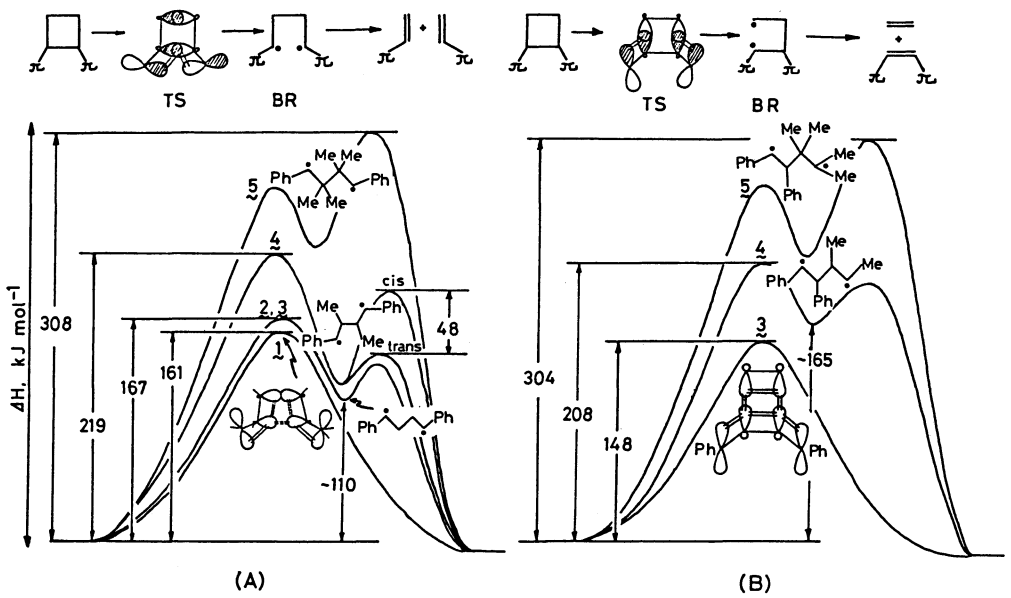


Fig. 5. Schematic potential surface diagrams for (A) the symmetric cleavage of **1**—**5** and (B) the unsymmetric cleavage of **3**—**5**. The numerals are enthalpy differences in kJ mol^{-1}.

nary carbon to inhibit the phenyl rings from taking the coplaner conformations required for benzylic stabilization. Similarly, large nonbonding interactions might destabilize **5**-BR$_b$ by a possible distortion of the Me_2C radical center from a planar conformation. More importantly, such large nonbonding interactions again impede the maximum overlap between the p orbitals of the radical centers and the C-C σ orbitals being broken. Such large steric effects on the destabilization of biradicals as well as on the biradical fragmentation should contribute to the very high values of $\Delta H_a^{\neq}$ and $\Delta H_b^{\neq}$. It is therefore suggested that the biradical fragmentation is rate determining in either the symmetric or the unsymmetric cleavage of **5**. Since the frequency factors are unusually large, extensive vibrational and rocking motions of C-Me are probably important in relieving large steric hindrance in the transition state.

Conclusion

Figure 5 shows schematic potential surface diagrams for the thermal reactions of the diarylcyclobutanes as a summary. The symmetric cleavage of **1** and the unsymmetric cleavage of **3** proceed by a concerted or concerted-like mechanism because of the small steric perturbation in realizing a "pericyclic" transition state, whereas 1,4-biradicals are involved in the other reactions. The net regiochemistry and the reactivities are controlled by both stable conformations and rotational mobilities of the aryl substituents associated with the π_a-σ_a* and π_s-σ_s* interactions occurring by thermal activation. Since the σ_a* character is more efficiently mixed in a bonding MO by through-bond coupling than the σ_s* character, the specific or selective symmetric cleavage of **1**—**3** should arise from the π_a-σ_a* interactions which are allowed without steric inhibition. In the cases of **4** and **5**, where the π_s-σ_s* interactions are sterically favorable, unsymmetric cleavage can occur competitively with the symmetric type. In conclusion, the steric-controlled orbital interactions are essential in the transition states of both the symmetric and the unsymmetric cleavage of the diarylcyclobutanes. For the reaction of **5**, however, the rate-determining step is the biradical fragmentation since nonbonding interactions are very large to destabilize both the biradicals and the transition states of the biradical fragmentation.

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References

1) C. Pac, *Pure Appl. Chem.*, **58**, 1249 (1986).
2) S. W. Benson,"Thermochemical Kinetics, Methods for the Estimation of Thermochemical Data and Rate Parameters," 2nd ed., John Wiley and Sons, New York (1976).
3) E. Schaumann and R. Ketcham, *Angew. Chem., Int. Ed. Engl.*, **21**, 225 (1982).
4) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., (1970).
5) J. S. Chikos, A. Annamalai, and T. A. Keiderling, *J. Am. Chem. Soc.*, **108**, 4398 (1986).
6) R. W. Carr, Jr. and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963).
7) H. R. Gerberich and W. D. Walters, *J. Am. Chem.*

Soc., **83**, 4884 (1961). J. A. Berson, D. C. Tompkins, and G. Jones, II, *ibid.*, **92**, 5879 (1970). Also see references cited in Refs. 2 and 3.

8) G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, **86**, 899 (1964). D. J. Trecker and D. H. Henry, *ibid.*, **86**, 902 (1964).

9) G. Jones, II, *J. Chem. Educ.*, **51**, 175 (1974). W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *J. Am. Chem. Soc.*, **94**, 1619 (1972). G. Jones, II and M. H. Williamson Jr., *ibid.*, **96**, 5617 (1974). L. M. Stephenson and T. A. Gibson, *ibid.*, **96**, 5624 (1974). Also see references cited in Refs. 2 and 3.

10) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 5246 (1974). G. A. Segal, *ibid.*, **96**, 7892 (1974).

11) R. Hoffman, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7091 (1970).

12) R. M. Moriarty, *Top. Stereochem.*, **8**, 271 (1974).

13) R. Hoffman and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971).

14) C. Pac, K. Mizuno, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **51**, 329 (1978).

15) L. A. Paquette and G. L. Thompson, *J. Am. Chem. Soc.*, **94**, 7127 (1972).

16) T. Imai and S. Nishida, *Chem. Lett.*, **1980**, 41.

17) G. Jones, II and V. L. Chow, *J. Org. Chem.*, **39**, 1447 (1974).

18) T. Majima, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **102**, 5265 (1980). C. Pac, T. Ohtsuki, Y. Shiota, S. Yanagida, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **59**, 1133 (1986). C. Pac, T. Fukunaga, Y. Go-An, T. Sakae, and S. Yanagida, *J. Photochem. Photobiol., A: Chemistry*, **41**, 37 (1987). C. Pac, Y. Go-An, and S. Yanagida, *Bull. Chem. Soc. Jpn.*, **62**1, 1951 (1989).

19) W. Metzner and D. Wendisch, *Justis Liebigs Ann. Chem.*, **730**, 111 (1969).

20) R. M. Dodson and A. G. Zielsske, *J. Org. Chem.*, **32**, 28 (1967).

21) O. L. Chapman and W. Radams, *J. Am. Chem. Soc.*, **90**, 2333 (1968).

22) L. D. Rodewald and C. H. dePuy, *Tetrahedron Lett.*, **1964**, 2951.

23) The heat of formation of **3** and 1,4-biradicals can be calculated according to the additivity rules of bond and group properties listed in tables of Ref. 2; ΔH_f^0 (**3**)=245.8 kJ mol^{-1}, ΔH_f^0 (PhĊHCH$_2$CH$_2$ĊHPh)=353.6 kJ mol^{-1}, and ΔH_f^0 (PhĊHCH(Ph)CH$_2$ĊH$_2$)=408.7 kJ mol^{-1}.

24) L. Salem and J. S. Wright, *J. Am. Chem. Soc.*, **91**, 5947 (1969).

25) R. Hoffman, *Acc. Chem. Res.*, **1**, 1 (1971).

26) K. Harano, T. Ban, M. Yasuda, E. Osawa, and K. Kanematsu, *J. Am. Chem. Soc.*, **103**, 2310 (1981).

27) a) D. A. Dougherty, H. B. Schlegel, and K. Mislow, *Tetrahedron*, **34**, 1411 (1978). b) D. A. Dougherty, W. D. Hownshell, H. D. Schlegel, R. A. Bell, and K. Mislow, *Tetrahedron Lett.*, **1976**, 3479.

28) K. Shima, J. Kimura, K. Yoshida, M. Yasuda, K. Imada, and C. Pac, *Bull. Chem. Soc. Jpn.*, **62**, 1934 (1989).

29) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).

30) Alternatively the C_C-C_D bond breaking would initially occur for the symmetric cleavage to generate 1,1,4,4-tetramethyl-2,3-diphenyl-1,4-butanediyl, which should be again unstable by large nonbonding interactions.