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# Photochemical Reactions of Aromatic Compounds. XLVI.[1] Stereochemical Reaction Courses in the Photolytic Ring-Cleavage Reactions of Diarylcyclobutanes: Implications of Conformation-Controlled Orbital Interactions in the Excited-State Chemistry

Chyongjin PAC,* Kazuyoshi GO-AN, and Shozo YANAGIDA
Department of Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565

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The photolyses of *cis-transoid-cis*-cyclobutadiindene (**1**), *cis*-2-phenylcyclobut[*a*]indene (**2**), *cis*-1,2-diphenylcyclobutane (**3**), the trans isomer (**4**), and its dimethyl (**5**) and tetramethyl (**6**) derivatives have been investigated to explore stereoelectronic factors controlling the excited-state reaction courses for the ring cleavages. The symmetric ring cleavage occurs regiospecifically in the cases of **1**—**3** and with 98% specificity in the case of **4**. The photolysis of **5** results in both the symmetric and the asymmetric cleavages in a ca. 1 : 3 ratio accompanied by substantial losses of stereointegrity in the olefin formation, and the regiospecific asymmetric cleavage occurs in the case of sterically more congested **6**. The ring-cleavage efficiencies systematically decrease in the order **1**>**2**>**3**>**4**>**5**>**6** and reveal negative temperature dependences, particularly in the cases of **1**, **5**, and **6**. The features of the reactions are in parallel with stable conformations and conformational mobilities of the aryl groups associated with different $\pi$-$\sigma$ orbital interactions, while the spectroscopic properties of the cyclobutanes are essentially identical with those of benzene chromophores with little electronic perturbation. The photolytic ring-cleavage reactions are discussed in terms of crossing from the localized $^1\pi,\pi^*$ state to a $\sigma^*$ hypersurface, in which conformation-controlled orbital interactions play important roles. The final products are formed via a pericyclic minimum which might be biradicaloid in nature.

Splitting of the cyclobutane rings has been providing an excellent probe for mechanistic and stereochemical studies[2-4] as well as a typical prototype for theoretical understanding of chemical reaction courses[5,6] because of simplicity of the net chemistry. Theories predict that [2+2] cycloreversions of cyclobutanes with stereoretention are forbidden in the ground state but are allowed in the $\sigma,\sigma^*$ state of the ring framework.[5,6] Extensive thermochemical and stereochemical data of thermal ring-splitting reactions of parent cyclobutane and alkyl derivatives are indeed accomodated with stepwise mechanisms involving 1,4-biradicals.[3,4] By contrast, little has been known on mechanistic and stereochemical aspects in the photochemistry of simple cyclobutanes bearing no particular chromophore, since no suitable methods are available to achieve the selective population of the ring $\sigma,\sigma^*$ state.[7]

Photochemical studies have therefore been carried out with chromophore-substituted cyclobutanes capable of being photoexcited by usual light sources. It was found that a few $\pi$-chromophore substituted cyclobutanes undergo the photolytic cycloreversions with complete stereoretention[8] or with only a minor loss of stereointegrity.[9,10] Another interesting observation of stereochemical significance is that the photolysis of $\pi$-substituted cyclobutanes results in the regiospecific or regioselective cleavage of a ring C–C bond in cases where a $\pi$ chromophore and a substituent vicinally attach to each end of this bond in the *cis configuration*. This is called "cis effect".[11]

A crucial question should emerge as to why the photo-excitation of a $\pi$ substituent can effect the specific or selective cleavage of the ring $\sigma$ framework that should proceed by way of a reaction hypersurface correlating with the ring $\sigma,\sigma^*$ state. Presumably, energy migration might occur from the photoexcited $\pi$ substituent to a specific C–C bond of the cyclobutane ring to bring about a surface crossing to the $\sigma,\sigma^*$ reaction hypersurface. However, there have been presented no convincing experimental data to explicate possible mechanisms and stereoelectronic requirements for such a surface crossing. Another important question is whether or not the photolytic ring cleavage of $\pi$-substituted cyclobutanes generally occurs with stereoretention. Systematic studies are certainly required to explore controlling factors in stereochemical reaction courses of photolytic ring-cleavage reactions of $\pi$-substituted cyclobutanes. The present paper deals with stereochemical and mechanistic details of the photolytic ring-cleavage reactions of diarylcyclobutanes **1**—**6**. We have found that the cyclobutanes reveal unique dependences of both the fluorescence bahavior and the reaction features on either stable conformations of the aryl substituents or temperature.

## Results

**Spectroscopic Properties.** Table 1 lists the absorption and fluorescence spectra in cyclohexane and the fluorescence quantum yields and lifetimes in acetonitrile at 20 °C together with the relevant quantities of toluene and indane used as reference compounds. The fluorescence spectra of **1**—**4** were taken by means of a photon-counting method, since the

Table 1. Spectroscopic Properties of the Cyclobutanes

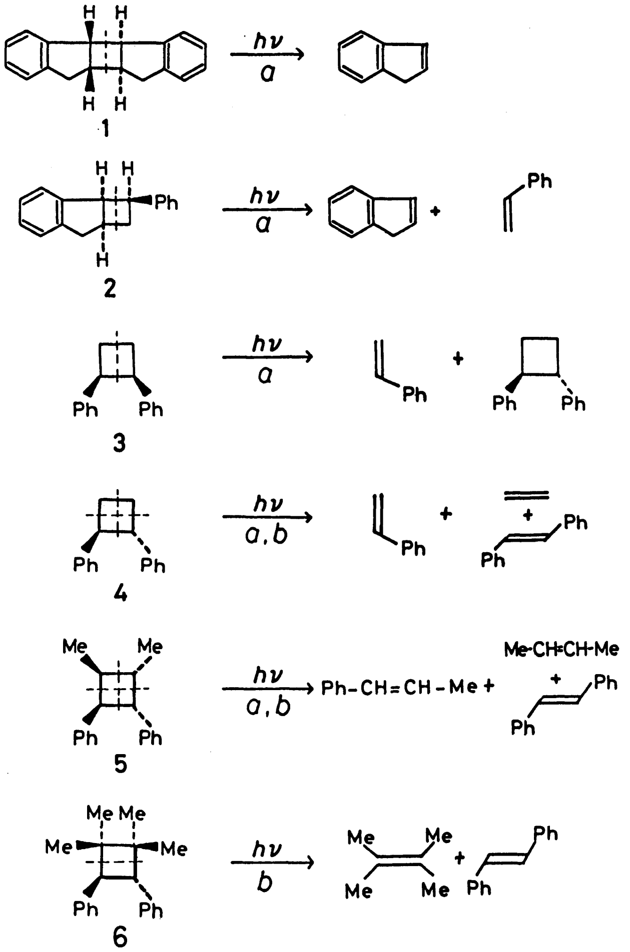
| Compound | $\lambda_{\max}{}^{a)}$/nm ($10^{-3}\varepsilon$) | $\lambda_{\max}^{F}{}^{b)}$/nm | $\phi_F{}^{c)}$ | $\tau_F{}^{d)}$/ns |
|---|---|---|---|---|
| **1** | 275 (4.3), 268 (4.0) | 276 | ca. 0.006 | e) |
| **2** | 275 (1.3), 267 (1.4) | 277 | ca. 0.007 | e) |
| **3** | 271 (0.3), 267 (0.4) | 272 | ca. 0.002 | e) |
| **4** | 270 (0.5), 262 (0.7) | 272 | ca. 0.01 | e) |
| **5** | 271 (0.6), 263 (0.7) | 271 | ca. 0.070 | 23 |
| **6** | 271 (0.8), 265 (0.9) | 271 | 0.14 | 22 |
| Indane | 274 (1.3), 267 (1.3) | 277 | f) | f) |
| Toluene | 270 (0.2), 263 (0.3) | 270 | 0.14 | 25 |

a) Absorption maxima in cyclohexane. b) Fluorescence maxima in cyclohexane. c) Fluorescence quantum yields in cyclohexane at 20 °C calculated from fluorescence intensities relative to that of toluene as standard. See Ref. 14. d) Fluorescence lifetimes in acetonitrile at 20 °C. e) The lifetimes were not be able to be determined, being presumably shorter than 1 ns; see text. f) Not determined.

Table 2. Temperature Dependences of Fluorescence Lifetimes$^{a)}$

| $T$/°C | $\tau_F$/ns | | |
|---|---|---|---|
| | **5** | **6** | Cumene |
| $-196^{b)}$ | 30 | 34 | |
| −20 | 40 | 40 | 44 |
| 2 | 30 | 28 | 28 |
| 20 | 23 | 22 | 18 |
| 30 | 20 | 19 | 14 |
| 40 | 18 | 16 | 11 |
| 50 | 14 | 13 | 8 |
| 60 | 12 | 10 | 6 |

a) Measured for degassed acetonitrile solution. b) In EPA (5:5:2 diethyl ether-isopentane-ethanol mixture) glasses. The lifetimes of **1**, **3**, and **4** in EPA glasses at 77 K are 10 ns, 9 ns, and 9 ns, respectively, but are presumed to be < 1 ns at ≥−20 °C; see text.



Scheme 1.

fluorescence efficiencies are very low and since usual measurements resulted in substantial contamination of the fluorescence from indene or styrene formed by the photolysis during the measurements. The absorption and fluorescence spectra of the cyclobutanes are essentially identical with those of indane or toluene, while the fluorescence quantum yields largely vary from $<10^{-2}$ for **1**—**3** to 0.14 for **6**, a value identical with that of toluene.

The fluorescence lifetimes were measured by means of single photon counting after deconvolution. In the cases of **1**—**4**, however, we obtained no reliable lifetime data at room temperature and even at −20 °C, probably because of very low emission efficiencies and very short lifetimes. At 77 K, the lifetimes could be determined to be 9—10 ns but are substantially shorter than those of **5**, **6**, and toluene (35 ns) at this temperature. Table 2 shows the fluorescence lifetimes of **5**, **6**, and cumene at various temperatures, which commonly decrease with the increase of temperature from −20 °C.

**Photolysis.** Irradiation of deaerated acetonitrile or cyclohexane solution of **1**—**6** at 254 nm gave exclusively the olefins formed by the symmetric (*a*) and/or the asymmetric (*b*) ring cleavages (Scheme 1); the isomerization of **3** to **4** occurred in a low efficiency. Material balances were well over 95% at <5% conversions and no other product was detected at all. Table 3 lists the reaction quantum yields ($\phi_a$ and $\phi_b$) and the *a*:*b* ratios at 20 °C. It was found that the reaction efficiencies vary with reaction temperature from 2 °C to 70 °C, particularly in the cases of **1**, **5**, and **6**, as shown in Table 4. The *a*:*b* ratios in the photolysis

Table 3. Reaction Quantum Yields for Photolysis of **1**—**6** at 254 nm[a)]

| Cyclobutane | $\phi_a$ | $\phi_b$[b)] | $a:b$ |
|---|---|---|---|
| **1** | 0.47 | | 100:0 |
| **2** | 0.37[c)]<br>0.32[d)] | | 100:0 |
| **3** | 0.17<br>0.006[e)]<br>(0.17, 0.014[e)] | | 100:0<br><br>100:0) |
| **4** | 0.14<br>(0.14 | 0.002<br>0.006 | 98:2<br>96:4) |
| **5** | 0.025<br>(0.020 | 0.070<br>0.070 | 26:74<br>22:78) |
| **6** | | 0.080 | 0:100 |

a) Obtained for acetonitrile and cyclohexane solution at 20 °C unless otherwise stated. In parentheses are the values for cyclohexane solution only in cases where they are different from those for acetonitrile solution. The quantum yields for the olefin formation from the symmetric cleavages of **1**, **3**, **4**, and **5** are the double of the listed values. b) For the stilbene formation. c) For the indene formation. d) For the styrene formation. e) For the isomerization to **4**.

Table 4. Temperature Dependences of Quantum Yields[a)]

| $T$/°C | $\phi_a$ | | | $\phi_a$ | $\phi_b$ | $\phi_b$ |
|---|---|---|---|---|---|---|
| | **1** | **3** | **4** | **5** | | **6** |
| 2 | 0.50 | 0.20 | 0.15 | 0.025 | 0.130 | 0.075 |
| 20 | 0.47 | 0.17 | 0.14 | 0.025 | 0.080 | 0.080 |
| 30 | 0.42 | | | 0.025 | 0.060 | 0.082 |
| 50 | 0.39 | | | 0.020 | 0.040 | 0.052 |
| 70 | 0.27 | 0.15 | 0.14 | 0.020 | 0.020 | 0.010 |

a) See footnotes in Table 3.

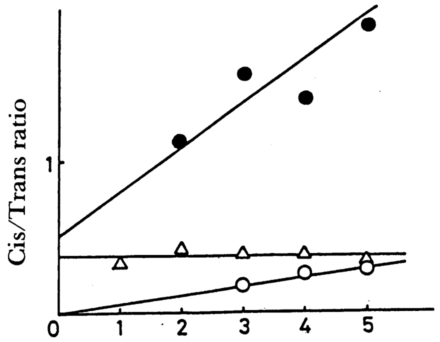


Fig. 1. Plots of cis-trans ratio vs. irradiation time for the formation of 1-phenylpropene (—●—), stilbene (—○—), and 2-butene (—△—) in the photolysis of **5** in acetonitrile at 20 °C; irradiation at 254 nm; [**5**]=0.01 M.

of **5** increase with an increase of temperature to reach 1 : 1 at 70 °C. In the case of **4**, the asymmetric cleavage is too minor to allow reliable determination of temperature-dependent $a:b$ ratios.

The olefin products from the photolysis of **5** are mixtures of the cis and trans isomers. The cis/trans ratios were determined at various irradiation times under keeping conversions below 3%. As shown in Fig. 1, the isomer ratios in formation of stilbene and 1-phenylpropene increase with irradiation time, probably due to secondary photoisomerization of the primary products. The values obtained by extrapolation of the plots to zero irradiation time should give the primary cis : trans ratios which are 0 : 100 in the stilbene formation and ca. 2 : 1 in the 1-phenylpropene formation. On the other hand, 2-butene was formed in a ca. 2 : 5 cis–trans ratio independently of irradiation time. Similarly *trans*-stilbene was confirmed to be the primary photoproduct from **6**.

## Discussion

**Mechanism.** The isomerization of **3** to **4** and the loss of stereointegrity in the olefin formation from **5** strongly suggest that the photolytic reactions of **3** and **5** proceed by way of a state or an intermediate susceptible to bond rotation. The acetone-photosensitized reaction of **3** gives styrene and **4** in respective quantum yields of 0.15 and 0.04[12)] and the styrene: **4** ratio in the thermal reaction of **3** is 2.3 : 1 at 300 K.[13)] Calculations using these values and the data in Table 3 indicate that the participation of either the triplet state of **3** or thermally equilibrated 1,4-diphenylbutane-1,4-diyl should be very minor, 15% or less the total reaction at best, provided that all the formation of **4** would arise only from triplet **3** or from the 1,4-biradical. Similarly, the involvement of a 1,4-biradical in the photolysis of **5** should be negligible since the cis : trans ratio in the 1-phenylpropene by the thermal reaction of **5** is 1 : 9 at 550 K and is calculated to be ca. 0 : 100 at 300 K.[13)] Furthermore, it was reported that either *trans*-2-heptene or dimethyl maleate does not affect the photolytic reaction of **3**.[12b)] We also confirmed that air saturation of solution exerts no effect on the photoreactions of **1**—**4** at all and slightly quenches those of **5** and **6**, probably due to oxygen quenching of the excited singlet state of the cyclobutanes.

The above arguments suggest that the photolytic ring-cleavage reactions of the cyclobutanes are not concerted but involve a reactive state responsible for the product formation, presumably a biradicaloid pericyclic minimum,[6)] which should be different from either the triplet state of the cyclobutanes or discrete 1,4-biradicals; this state is denoted as "X" for convenience. Since the absorption and fluorescence spectra of the cyclobutanes are essentially identical with those of alkylbenzenes, the spectroscopic excited state is the $^1\pi,\pi^*$ state of the aryl substituent in which little electronic perturbation by the cyclobutane ring occurs. The basic mechanistic pathways of the photoreactions are shown in Eqs. 1—6 where Eq. 3 involves temperature-independent photophysical processes (e.g., internal conversion and intersystem crossing) and an activated nonradiative process. The reaction quantum yield ($\phi_r$) is represented by Eq. 7 where $\alpha$ is the partition coefficient for the product formation from X.

$$\mathrm{M} \xrightarrow{h\nu} {}^1\mathrm{M}^*({}^1\pi,\pi^*) \tag{1}$$

$$ {}^1\mathrm{M}^* \xrightarrow{k_\mathrm{F}} \mathrm{M} + h\nu_\mathrm{F} \tag{2}$$

$$ {}^1\mathrm{M}^* \xrightarrow{k_\mathrm{d}} \mathrm{M} \tag{3}$$

$$ {}^1\mathrm{M}^* \xrightarrow{k_\mathrm{r}} \mathrm{X} \tag{4}$$

$$\mathrm{X} \xrightarrow{\alpha} \text{product} \tag{5}$$

$$\mathrm{X} \xrightarrow{1-\alpha} \mathrm{M} \tag{6}$$

$$\phi_\mathrm{r} = \alpha k_\mathrm{r}/(k_\mathrm{F} + k_\mathrm{d} + k_\mathrm{r}) = \alpha k_\mathrm{r}\tau_\mathrm{s} \tag{7}$$

**Analysis of Temperature Dependence.** It is known that fluorescence lifetimes of benzene and alkylbenzenes decrease with an increase of temperature as the consequence arising from the involvement of an activated pathway in the nonradiative decay.[14] This pathway is attributed to a surface crossing from the excited singlet state to an isomer surface, from which the starting ground-state arene is mostly regenerated along with very inefficient formation of an isomer such as fulvene. At any rate this mechanism should be responsible for the temperature dependence of fluorescence lifetimes of **5** and **6** since $k_\mathrm{r}$ appears to be smaller by an order of magnitude than $\tau_\mathrm{s}^{-1}$, as calculated by Eq. 7. The temperature dependence can therefore be analyzed by the use of Eq. 8 in which $k_\mathrm{d}^0$ represents the rate constant for overall temperature-independent photophysical processes.

$$1/\tau_\mathrm{s} = k_\mathrm{d}^0 + A_\mathrm{d}\exp(-\Delta H_\mathrm{d}^{\neq}/RT) \tag{8}$$

Figure 2 shows best-fit plots of $\log(\tau_\mathrm{s}^{-1} - k_\mathrm{d}^0)$ vs. $1/T$ for cumene, **5**, and **6**, from which $A_\mathrm{d}$ and $\Delta H_\mathrm{d}^{\neq}$ are obtained. Table 5 lists the values of $k_\mathrm{d}^0$, $A_\mathrm{d}$, and $\Delta H_\mathrm{d}^{\neq}$ together with the reported quantities for the cis-trans-cis and all-trans isomers of tetraphenylcyclobutane[15] for comparison. These values fall in those reported for benzene and toluene.[14] It is therefore evident that the spectroscopic excited singlet state of **5** and **6** is just the ${}^1\pi,\pi^*$ state of an isolated phenyl substituent not only in the electronic properties but also in the dynamic decay pathways, Eqs. 2 and 3. This appears to be again true for **1**—**4**, since the electronic spectra reveal no perturbation of the ${}^1\pi,\pi^*$ state of the aryl substituent; the very low emission efficiencies should be due to large $k_\mathrm{r}$.

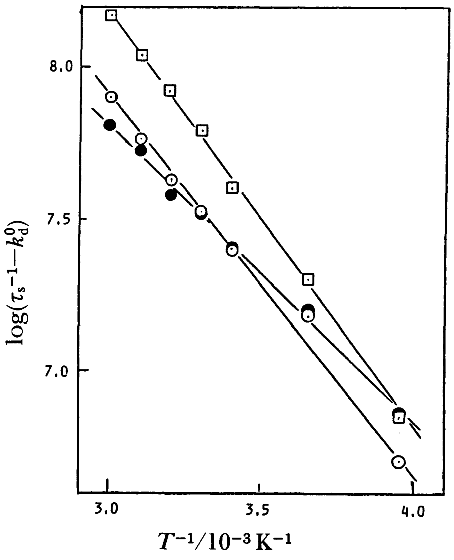


Fig. 2. Best-fit plots of $\log(\tau_\mathrm{s}^{-1} - k_\mathrm{d}^0)$ vs. $T^{-1}$ for **5** (—●—), **6** (—○—), and cumene (—□—); data are from Table 2.

Table 5. Preexponential Factor $A_\mathrm{d}$ and Activation Barrier $\Delta H_\mathrm{d}^{\neq}$ for Activated Nonradiative Decay[a)]

| Compound | $k_\mathrm{d}^0/10^7\,\mathrm{s}^{-1}$ | $A_\mathrm{d}/10^{11}\,\mathrm{s}^{-1}$ | $\Delta H_\mathrm{d}^{\neq}$/ kcal mol$^{-1}$ |
|---|---|---|---|
| Cumene | 1.6 | 21.0 | 6.3 |
| **5** | 1.8 | 0.65 | 4.6 |
| **6** | 2.0 | 2.6 | 5.3 |
| *c*-*t*-*c*-TPCB[b,c)] | 1.5 | 4.2 | 3.8 |
| *all*-*t*-TPCB[b,d)] | 1.5 | 0.14 | 2.4 |

a) Obtained by analysis of the data in Table 2; see Fig. 2 and text. b) Reported values for tetraphenylcyclobutane; see Ref. 15. c) *r*-1,*c*-2,*t*-3,*t*-4-Tetraphenylcyclobutane. d) All-trans isomer.

Analysis of the temperature dependences of quantum yield might provide a clue to explore the dynamic reaction pathways from the ${}^1\pi,\pi^*$ state. It can be presumed that no activated pathways participate after the decay from X to the ground-state surface, since a 1,4-biradical minimum is unlikely to be involved in the ring-cleavage reactions as already mentioned. Calculations according to Eq. 7 using the observed lifetimes and quantum yields give the $\alpha k_\mathrm{r}$ values at 2—70 °C for **5** and **6**; the lifetimes at 70 °C were estimated from the plots in Fig. 2. Plots of $\log(\alpha k_\mathrm{r})$ vs. $1/T$ give positive slopes for the asymmetric clevage of **5** and for the ring cleavage of **6** at ≥50 °C, whereas the symmet-

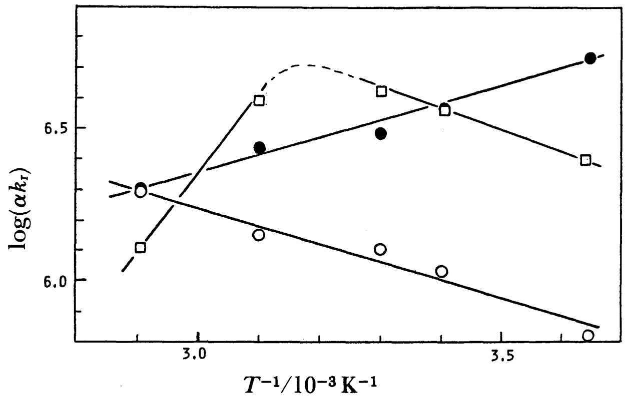


Fig. 3. Plots of $\log(\alpha k_\mathrm{r})$ vs. $T^{-1}$ for the symmetric (—○—) and asymmetric (—●—) cleavages of **5** and for the asymmetric cleavage of **6** (—□—); data are from Tables 2 and 4.

ric cleavage of **5** and the ring cleavage of **6** at lower temperatures reveal plots of usual negative slopes, as shown in Fig. 3.

The negative temperature dependences might arise from $\alpha$ or from $k_r$ as the consequence of increasing regeneration of the starting cyclobutane with the increase of temperature through an activated pathway along the excited-state potential surface. We can assume two possibilities, i.e., (1) thermal regeneration of $^1M^*$ from another intermediate state "Y" involved prior to X in the mechanistic sequence and (2) pseudo equilibrium between an early pericyclic minimum $X_1$ and another more stable one $X_2$ which decay to the starting cyclobutane and to the olefin products respectively. In the latter case, $X_1$ is thermally repopulated from $X_2$ in which losses of stereo-integrity should occur. It can therefore be presumed that the isomerization of **5** might increasingly occur with the increase of temperature. In order to confirm possible formation of an isomer of **5** (e.g., *r*-1,*c*-2-dimethyl-*c*-3,*t*-4-diphenylcyclobutane), we extensively carried out VPC analyses using different columns for photolysates of **5** irradiated at 60 °C and $^1H$ NMR analyses for cyclobutane fractions obtained by column chromatography of the photolysates. However, no indication was obtained for the formation of any isomer of **5**.

Accordingly, we choose the former mechanism to analyze the observed temperature dependences under the assumption that $\alpha$ is independent of temperature, though there is no direct evidence to discard the other mechanism. On the basis of this assumption, Eq. 4 is replaced by Eqs. 9 and 10, and $k_r$ is represented by Eq. 11. The positive slopes of the plots in Fig. 3 imply that $k_{-r} > k_c$, thus giving lower limits of the difference between the enthalpy change of Eq. 9

$$^1M^* \underset{k_{-r}}{\overset{k_r'}{\rightleftharpoons}} Y \qquad (9)$$

$$Y \xrightarrow{k_c} X \qquad (10)$$

$$k_r = k_r'[k_c/(k_{-r}+k_c)] = k_c[k_r'/(k_{-r}+k_c)] \qquad (11)$$

and the activation enthalpy of Eq. 10, $(\Delta H_{-r}^{\neq} - \Delta H_r^{\neq}) - \Delta H_c^{\neq}$, which are 3±1 kcal mol$^{-1}$ (1 kcal=4.184 kJ) for the asymmetric cleavage of **5** and roughly 10—12 kcal mol$^{-1}$ for the ring cleavage of **6**. On the other hand, the plots of negative slope in Fig. 3 indicate that $(\Delta H_{-r}^{\neq} - \Delta H_r^{\neq}) \gg \Delta H_c^{\neq}$ or $\Delta H_c^{\neq}=0$, giving $\Delta H_r^{\neq}$ and the preexponential factor $A_r$ for the symmetric cleavage of **5** and lower limits of $\Delta H_r^{\neq}$ and $A_r$ for the ring cleavage of **6**, which are listed in Table 6 together with the relevant values reported for the photolysis of tetraphenylcyclobutane.[15]

In the cases of **1—4**, it is reasonable to presume that $k_r \geq 5\times10^8$ s$^{-1} \gg (k_F+k_d)$. In this regard, it should be noted that the fluorescence lifetimes of **1**, **3**, and **4** are 9—10 ns at 77 K, still much shorter than those of **5** and **6** which are similar to that of toluene. Moreover, we confirmed that irradiation of **1—4** in EPA glasses at 77 K gives the corresponding olefins[11] while little photolytic ring cleavage of **5** and **6** occurs under similar conditions. It is therefore implied that $\Delta H_r^{\neq} < 3$ kcal mol$^{-1}$ and $A_r > 10^{11}$ s$^{-1}$ for the symmetric cleavage of **1—4**. Since $k_r \gg k_d$, the negative temperature dependence of $\phi_r$ in the photolysis of **1** can be analyzed according to Eq. 12. A best-fit plot of $\log[(\alpha-\phi_r)/\phi_r]$ vs. $1/T$ obtains by assuming $\alpha=0.55$ as shown in Fig. 4, thus giving the value of $(\Delta H_{-r}^{\neq} - \Delta H_c^{\neq})$ which is 7±1 kcal mol$^{-1}$.

$$(\alpha-\phi_r)/\phi_r = k_{-r}/k_c \qquad (12)$$

Table 6. Preexponential Factor $A_r$ and Activation Barrier $\Delta H_r^{\neq}$ for the $^1M^* \rightarrow Y$ Process[a)]

| Cyclobutane | $A_r$/s$^{-1}$ | $\Delta H_r^{\neq}$/kcal mol$^{-1}$ |
|---|---|---|
| **1—4** | $>10^{11}$ | $<3$ |
| **5**[b)] | $(7\pm2)\times10^{7}$ [c)] | 2.4±0.2 |
| **6** | $\geq4\times10^{8}$ [c)] | $\geq3$ |
| *c-t-c*-TPCB[d)] | $2.0\times10^{11}$ | 3.5 |
| *all-t*-TPCB[d)] | $7.9\times10^{10}$ | 3.8 |

a) Obtained by analysis of the data in Tables 2 and 3; see text. b) For the symmetric cleavage. c) Calculated by assuming $\alpha$=0.5. d) Reported values for tetraphenylcyclobutanes; see footnote in Table 5 and Ref. 15.

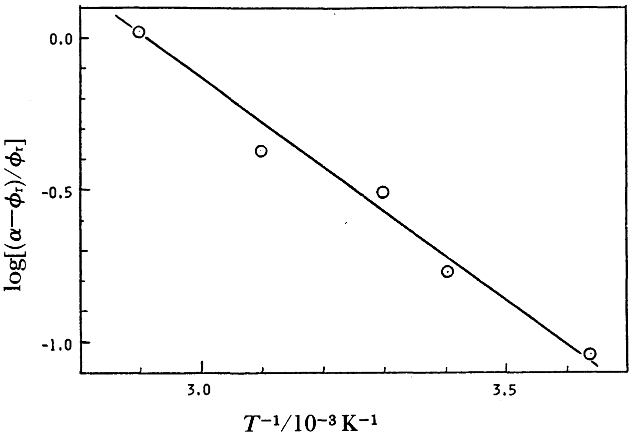


Fig. 4. A best-fit plot of $\log[(\alpha-\phi_r)/\phi_r]$ vs. $T^{-1}$ obtained by assuming $\alpha$=0.55 for the photolysis of **1**; data are from Table 4.

**Stereochemical Reaction Courses Associated with $\pi$-$\sigma$ Orbital Interactions.** We previously reported that through-bond coupling between vicinal $\pi$ electron systems across the cyclobutane-ring $\sigma$ framework plays essential roles in ring-splitting reactions of diarylcyclobutanes by redox photosensitization,[16] by exciplex photosensitization,[17] by electron-transfer photosensitization,[18] and by $\gamma$ radiolysis.[19] Although an essential mechanistic event in those reactions is commonly the population of a positive charge by the complete or partial removal of an electron, it can be presumed that the regiochemistry and reactivities in the present photolytic reactions of the cyclobutanes are controlled by different $\pi$-$\sigma$ orbital interactions.

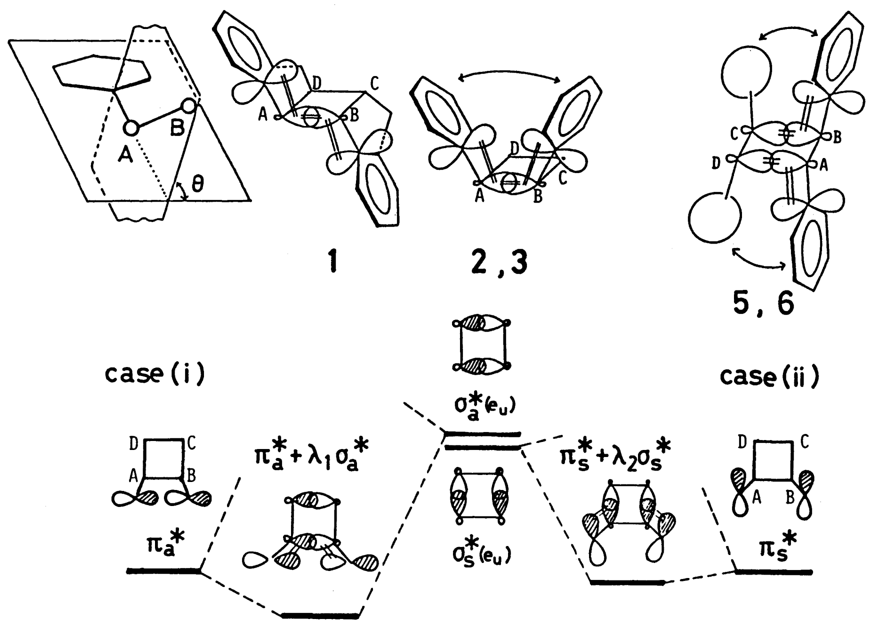


Fig. 5. Top: Stable conformations of the aryl substituents associated with favorable orbital interactions; $\theta \approx 90°$ for case (i) and $\theta \approx 0°$ for case (ii). Bottom: Schematic representation of $\pi_a^*$-$\sigma_a^*$ and $\pi_s^*$-$\sigma_s^*$ interactions.

Figure 5 shows different conformational situations of the aryl ring for $\pi$-$\sigma$ orbital interactions (case (i) and case (ii)) together with the notation of the carbon atoms of the cyclobutane ring.

In case (i) where torsional angles ($\theta$) between the aryl ring and the ipso C-$C_A$-$C_B$ plane are ca. 90°, the $\pi$ orbitals can maximally overlap with the $C_A$-$C_B$ $\sigma$ orbitals. Such conformational situations are indeed realized in **1** by the rigid tricyclic structure as well as in **2** and **3** by steric repulsion between the bulky vicinal aryl substituents in the cis configuration, as demonstrated by the X-ray crystallographic analysis[20] as well as by molecular models. It is evident that conformational rigidity decreases in the order of **1**>**2**>**3**. In case (ii) where $\theta \approx 0°$, the $\pi$ orbitals can not overlap with the orthogonal $C_A$-$C_B$ $\sigma$ orbitals but favorably with the $C_A$-$C_D$ and $C_B$-$C_C$ $\sigma$ orbitals. The X-ray crystallographic analysis of **6** and *r*-1,*t*-2-bis(hydroxymethyl)-*t*-3,*c*-4-diphenylcyclobutane, an analogue of **5**, demonstrates that $\theta \leq 11.3°$ due to nonbonding interactions between the cis substituents.[20] It is therefore evident that conformations of **5** and **6** fall in case (ii) though **5** is more mobile than the very rigid cyclobutane, **6**. On the other hand **4** can take either case (i) or case (ii) conformations. These conformational situations of the cyclobutanes associated with orbital interactions are well in parallel with the observed regiochemistry in the photolytic ring-cleavage reactions. However, effects of orbital interactions on the present photochemistry should be dynamic in nature since the spectroscopic properties of the cyclobutanes are essentially identical with those of alkylbenzenes with little electronic perturbation. It can be presumed that $\pi$-$\sigma$ orbital interactions play important roles in the mechanistic sequence, $^1M^* \rightarrow Y \rightarrow X$.

For qualitative considerations on roles of orbital interactions in the stereochemical reaction courses, we use Salem's $\sigma_s^*$ and $\sigma_a^*$ orbitals of cyclobutane[21] and the $\pi^*$ combinations, $\pi_s^* \equiv (\pi_A^*, \pi_B) + (\pi_A, \pi_B^*)$ and $\pi_a^* \equiv (\pi_A^*, \pi_B) - (\pi_A, \pi_B^*)$; subscript s or a represents the symmetric or antisymmetric character with respect to two-fold rotation or reflection. Orbital interactions can occur between $\pi_a^*$ and $\sigma_a^*$ or between $\pi_s^*$ and $\sigma_s^*$ to give a half-filled molecular orbital, $\pi_a^* + \lambda_1\sigma_a^*$ or $\pi_s^* + \lambda_2\sigma_s^*$ each,[22] as shown in Fig. 5. It should be however noted that the $\pi_a^*$-$\sigma_a^*$ interactions lead to through-bond coupling between the vicinal $\pi$ electron systems without large molecular distortions to stabilize $\pi_a^* + \lambda_1\sigma_a^*$, i.e., $\lambda_1 > 0$. In other words the $\pi_a^*$-$\sigma_a^*$ interactions can efficiently occur along the reaction coordinate to bring about delocalization of the photoexcitation of $^1M^*$ over the $\pi_A$-$\sigma_A$-$\sigma_B$-$\pi_B$ orbital array involved in through-bond coupling, thus facilitating the crossing from $^1M^*$ to a $\sigma,\sigma^*$ reaction hypersurface for the symmetric cleavage. On the other hand the $\pi_s^*$-$\sigma_s^*$ interactions are ineffective to through-bond coupling because of little overlap between the $C_A$-$C_D$ and the $C_B$-$C_C$ $\sigma$ orbitals in $\sigma_s^*$, i.e., $\lambda_2 \approx 0$ without large structure changes. It can therefore be predicted that the crossing from $^1M^*$ to a reaction hypersurface for the asymmetric cleavage is slow, since energy migration from the photoexcited aryl group to the cyclobutane-ring $\sigma$ framework through the $^*\pi_s$-$\sigma_s^*$ interactions should be inefficient.

The above molecular-orbital arguments provide a

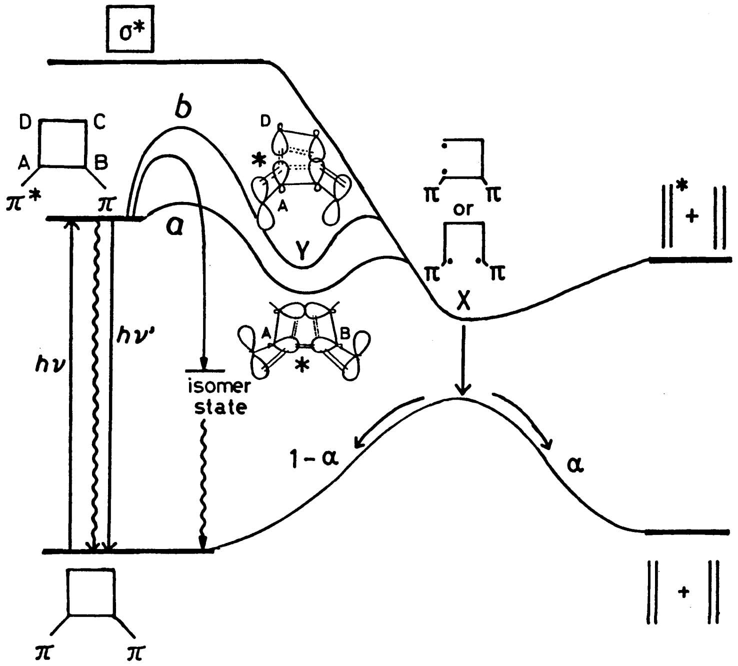


Fig. 6. Schematic reaction surfaces for the photolytic ring cleavages of diarylcyclobutanes in *a* and *b* directions involving the sequential pathways $^1M^*$ (localized $^1\pi,\pi^*$ state)→Y($\pi^*$-$\sigma^*$ state)→$\sigma,\sigma^*$ reaction hypersurface→X(biradicaloid state)→product.

rational to interpret the conformation-controlled regiochemistry and the different reactivities of the symmetric and asymmetric cleavages. In the cases of **1**—**3** where only the $\pi_a^*$-$\sigma_a^*$ interactions are conformationally allowed, the low activation barriers and the large $A_r$ values for the $^1M^*\rightarrow Y$ process suggest that the $\sigma_a^*$ character should be significantly mixed in the transition state without large structure changes. On the other hand, the slow ring cleavage of **6** in *b* direction suggests that mixing of the $\sigma_s^*$ character should be inefficient even though only the $\pi_s^*$-$\sigma_s^*$ interactions are conformationally allowed. Since $\Delta H_r^{\neq}>3$ kcal mol$^{-1}$ and $A_r \ll 10^{11}$ s$^{-1}$ for **6**, significant mixing of the $\sigma_s^*$ character would require highly restricted molecular motions in the transition state of the $^1M^*\rightarrow Y$ process, e.g., elongation of the $C_A$-$C_D$ and $C_B$-$C_C$ bonds and concurrent shortening of the $C_A$-$C_B$ bond with keeping $\theta\approx 0°$. In the cases of **4** and **5**, therefore, more effective mixing of the $\sigma_a^*$ character may allow the regioselective cleavage of **4** in *a* direction irrespective of mobile conformations and may counterbalance the conformational disadvantage of the $\pi_a^*$-$\sigma_a^*$ interactions in **5**. The low $A_r$ value for the symmetric cleavage of **5** indeed demonstrates that vibrational and rotational motions are extremely restricted in the transition state. Although details of Y still remain unknown, stabilization by the $\pi_a^*$-$\sigma_a^*$ or $\pi_s^*$-$\sigma_s^*$ orbital interactions might be important in Y where structures of the cyclobutanes would be different from those in $^1M^*$. In this regard it should be noted that $\Delta H_r^{\neq}<\Delta H_c^{\neq}$ for **1** and **6** but $\Delta H_r^{\neq}\approx\Delta H_c^{\neq}$ for **3** and **4**. Presumably the rigid structures of **1** and **6** might freeze maximum orbital overlaps to stabilize Y to substantial degrees. On the other hand conformational mobilities of **3** and **4** would be unfavorable for stabilization of Y since the orbital interactions can slip out with small molecular motions, e.g., rotational and rocking motions of the phenyl rings and puckering motions of the cyclobutane ring. At any rate significant mixing of the $\sigma_a^*$ or $\sigma_s^*$ character in Y is certainly favorable for the crossing from Y to a $\sigma,\sigma^*$ reaction hypersurface for a molecule to reach a biradicaloid pericyclic minimum X,[6] in which the $C_A$-$C_B$ or the $C_A$-$C_D$ (or $C_B$-$C_C$) bond is elongated enough for substantial bond rotation to occur.

## Conclusion

Figure 6 shows schematic reaction surfaces for the photolytic ring cleavages of **1**—**6** as a summary. The mechanism involves the sequential pathways, $^1M^*$ (localized $^1\pi,\pi^*$ state) → Y ($\pi_a^*$-$\sigma_a^*$ or $\pi_s^*$-$\sigma_s^*$ state) → $\sigma,\sigma^*$ reaction hypersurface → X (biradicaloid state) → product. The net regiochemistry is determined in the $^1M^*$ → Y process depending on conformations of the aryl substituents associated with the orbital interactions. Since the $\sigma_a^*$ character is effectively mixed by through-bond interaction without large structure changes, the $^1M^*\rightarrow Y\rightarrow X$ processes can efficiently occur in cases where the $\pi_a^*$-$\sigma_a^*$ interactions are conformationally allowed. On the other hand, the asymmetric cleavage is inherently slow as the consequence of inefficient mixing of the $\sigma_s{}^*$ character. In other words the specific or selective asymmetric ring cleavage can occur only in cases where the aryl rings are sterically inhibited to take case (i) conformations. In short the "cis effect" should be the consequence arising from steric control of the different orbital interactions.

The present investigation may provide a general concept for the understanding of both regioselectivities and reactivities in photolytic bond-cleavage reactions of various $\pi$-substituted cyclobutanes11,23—25) and, perhaps, of diarylethane-type compounds. Synthetic implications of the present investigation may be given by elegant preparation of bullvalene,26) pentalene derivatives,27) cyclobutadiene,28) and azetidinone29) from photolyses of rigid polycyclic cyclobutanes with $\pi$ chromophores, since the regiochemistry is that expected from specific orbital interactions imposed by the rigid structures.

## Experimental

Ultraviolet absorption spectra were recorded on a Hitachi 220-A UV spectrophotometer and fluorescence measurements were performed on a Hitachi 850 spectrofluorometer after correction for the spectral response of the instrument. Fluorescence lifetimes were determined on a Horiba NAES-1100 time-resolved spectrofluorometer. Vapor-phase chromatographic analyses were performed on a Shimadzu GC-7A gas chromatograph using a 2-m column of 10% PEG 20M on Shimalite NAW-101, a 3-m column of 2% OV 17 on Chromosorb W AW-DMCS, and a 5-m column of 25% ODPN on Shimalite NAW-101.

**Materials.** Spectrograde cyclohexane (Wako Pure Chemicals) was used after distillation. Reagent-grade acetonitrile was refluxed over $P_2O_5$ and then distilled. This procedure was repeated three times, and then the acetonitrile was distilled from $CaH_2$ prior to use. The cyclobutanes were prepared according to the literature methods; *cis-transoid-cis*-cyclobuta[1,2-*a*;4,3-*a'*]diindene (**1**),30) *endo*-2-phenyl-2,2a, 7,7a-tetrahydro-1*H*-cyclobut[*a*]indene (**2**),16) *cis*-1,2-diphenylcyclobutane (**3**),31) *trans*-1,2-diphenylcyclobutane (**4**),31) *r*-1,*t*-2-dimethyl-*t*-3,*c*-4-diphenylcyclobutane (**5**),17) and 1,1,2,2-tetramethyl-*trans*- 3,4-diphenylcyclobutane (**6**).32) Purification was achieved by repeated recrystallization from methanol for **1**, **2**, and **3** or from hexane for **6**, whereas **4** and **5** were distilled in vacuo. Vapor-phase chromatographic analyses of the purified cyclobutanes revealed that **4** includes the cis isomer in ca. 5% whereas the other cyclobutanes are virtually pure (> 99%).

**Photolysis.** A cyclohexane or acetonitrile solution of **1**—**6** (0.01 mol dm$^{-3}$) in a quartz cuvette was flushed with a gentle stream of Ar, placed in a temperature-regulated water bath, and then irradiated with an Eikosha POL-100 low-pressure mercury arc lamp through a Toshiba UV-D 25 glass filter which cuts off the 185-nm emission from the light source. The progress of the photoreaction was followed by vapor-phase chromatography. A potassium trioxalatoferrate(III) actinometer was used for the determination of quantum yields. It was confirmed that the observed quantum yields for the photoreactions of **1** and **5** are almost constant within experimental errors (± 5%) independently of concentration from $5\times10^{-3}$ to $5\times10^{-2}$ mol dm$^{-3}$.

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### References

1) Part XLV. C. Pac, T. Fukunaga, Y. Go-An, T. Sakae, and S. Yanagida, *J. Photochem. Photobiol. A: Chemistry*, **41**, 37 (1987).

2) C. Pac, *Pure Appl. Chem.*, **58**, 1249 (1986).

3) S. W. Benson, "Thermochemical Kinetics, Methods for the Estimation of Thermochemical Data and Rate Parameters," 2nd ed., John Wiley & Sons, New York (1976).

4) E. Schaumann and R. Ketcham, *Angew. Chem., Int. Ed. Engl.*, **21**, 225 (1982).

5) R. B. Woodward and R. Hoffmann,"The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/ Bergstr (1970).

6) W. Gerharts, R. D. Poshusta, and J. Michl, *J. Am. Chem. Soc.*, **98**, 6427 (1976); J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).

7) W. Adam and T. Oppenlander, *Angew. Chem., Int. Ed. Engl.*, **23**, 641 (1984).

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

9) R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, **13**, 45 (1980).

10) L. A. Paquette and G. L. Thompson, *J. Am. Chem. Soc.*, **94**, 7172 (1972).

11) G. Kaupp, *Angew. Chem.*, **84**, 741 (1974); G. Kaupp and M. Stark, *Chem. Ber.*, **110**, 3084 (1977).

12) a) Our quantum yields for the present direct photolysis of **3** and **4** and for the acetone-photosensitized reactions are larger by an order of magnitude than the values reported by Jones and Chow.12b) b) G. Jones, II and V. L. Chow, *J. Org. Chem.*, **39**, 1447 (1974).

13) a) M. Yasuda, K. Yoshida, K. Shima, and C. Pac, *Bull. Chem. Soc. Jpn.*, **62**, 1943 (1989). b) For the thermal reaction of **3**, $\Delta H^{\neq}=40.0$ kcal mol$^{-1}$ and $\log A=14.0$ for the styrene formation and $\Delta H^{\neq}=38.5$ kcal mol$^{-1}$ and $\log A=12.8$ for the isomerization to **4**, and $(\Delta H_{\mathrm{cis}}{}^{\neq}-\Delta H_{\mathrm{trans}}{}^{\neq})=10.6$ kcal mol$^{-1}$ and $\log(A_{\mathrm{cis}}/A_{\mathrm{trans}})=3.4$ for the 1-phenylpropene formation from **5**.13a)

14) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970), Chap. 5 and pp. 240—248.

15) H. Shizuka, I. Seki, T. Morita, and T. Iizuka, *Bull. Chem. Soc. Jpn.*, **52**, 2074 (1979).

16) T. Majima, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **102**, 5265 (1980) and *J. Chem. Soc., Perkin Trans. 1*, **1980**, 2705; C. Pac, J. Kubo, T. Majima, and H. Sakurai, *Photochem. Photobiol.*, **36**, 2773 (1982).

17) C. Pac, T. Ohtsuki, Y. Shiota, S. Yanagida, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **59**, 1133 (1986).

18) C. Pac, T. Ohtsuki, T. Fukunaga, Y. Yanagida, and H. Sakurai, *Chem. Lett.*, **1985**, 1855. Also see Refs. 1 and 2.

19) C. Pac, T. Majima, S. Takamuku, and H. Sakurai, *Chem. Lett.*, **1979**, 1149; *Nippon Kagaku Kaishi*, **1984**, 1880.

20) K. Shima, J. Kimura, K. Yoshida, M. Yasuda, and C. Pac, *Bull. Chem. Soc. Jpn.*, **62**, 1943 (1989).

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

22) R. Hoffmann, *Acc. Chem. Res.*, **1**, 1 (1971).

23) G. Kaupp and E. Jostkleigrewe, *Angew. Chem., Int. Ed. Engl.*, **15**, 779 (1976).

24) S. Takamuku and W. Schnabel, *Chem. Phys. Lett.*, **69**, 399 (1980).

25) N. Yonezawa, T. Yoshida, and M. Hasegawa, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1083.

26) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

27) K. Hafner, R. Dönges, E. Goedecke, and R, Kaiser, *Angew. Chem.*, **85**, 362 (1973).

28) S. Masamune, M. Suda, H. Ona, and L. M. Leichter, *J. Chem. Soc., Chem. Commun.*, **1972**, 1268.

29) G. Kretschner and R. N. Warrener, *Tetrahedron Lett.*, **1975**, 1335.

30) W. Metzner and D. Wendisch, *Liebigs Ann. Chem.*, **1980**, 1583.

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

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