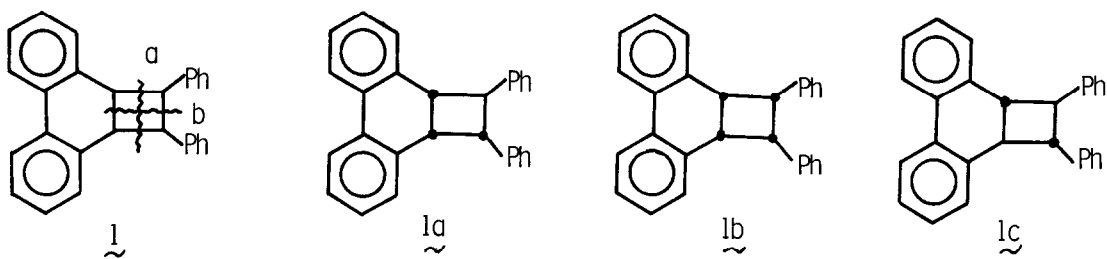


ORIENTATION SELECTIVE BOND CLEAVAGE REACTIONS OF BIPHENYL-FUSED  
1,2-DIPHENYLCYCLOBUTANES INITIATED BY ELECTRON TRANSFER<sup>1</sup>

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**Abstract:** Biphenyl-fused 1,2-diphenylcyclobutanes underwent orientation selective bond cleavage in the photosensitized reactions using DCA as a sensitizer or aminium cation radical catalyzed reactions.

In recent years much attention has been focused on the electron transfer bond cleavage of cyclobutanes in which cation radicals of cyclobutanes are involved as intermediates to undergo bond cleavage reactions.<sup>2</sup> Photosensitized bond cleavage reactions of 1,2-diaryl substituted cyclobutanes have been studied in detail by Pac and Sakurai et al.<sup>3</sup> who pointed out that the interaction between the two aryl groups through the cyclobutane bond is essential for the occurrence of bond cleavage. Biphenyl-fused cyclobutanes 1 seem to be good model compounds to establish the structure-reactivity relationship in electron-transfer bond cleavage reactions since they are expected to undergo two different types of cleavage, i.e., path a and path b, depending on the through-bond interaction. We wish to describe here the orientation selective bond cleavage reactions initiated by electron transfer.



According to the reported methods, cyclobutanes 1a was synthesized by photochemical ( $2\pi + 2\pi$ ) cycloaddition of phenanthrene to trans-stilbene,<sup>4</sup> and 1b, c were prepared by thermal and photochemical isomerization of 2,2'-distyryl-biphenyl (2), respectively.<sup>5</sup> The half-wave oxidation potentials of 1a-c were measured by cyclic voltammetry.

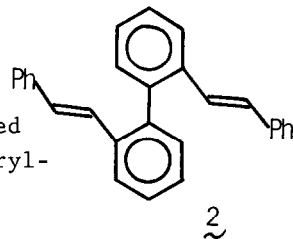


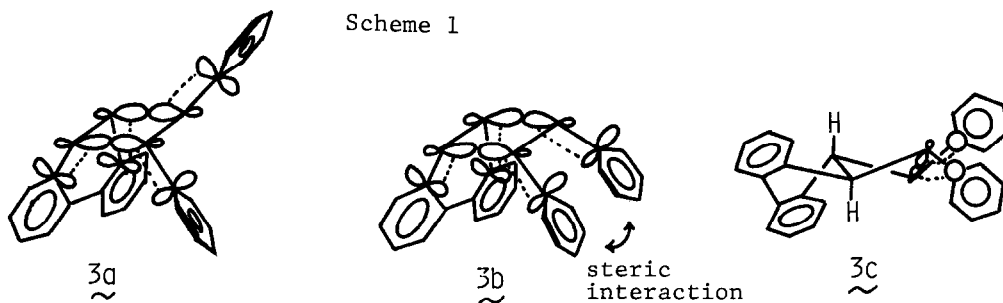
Table 1. Oxidation potentials and free-energy change ( $\Delta G$ ) of cyclobutanes 1a-c, and quenching rate constants of 1a,c

Compd	$E_{1/2}^{\text{ox}} / \text{V vs. SCE}^{\text{a}}$	$k_q / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}^{\text{b}}$	$\Delta G / \text{kJ mol}^{-1}$
<u>1a</u>	1.45, <sup>c)</sup> 1.64 <sup>c)</sup>	$9.9 \times 10^9$	-50.2
<u>1b</u>	1.64 <sup>c)</sup>	—	-31.8
<u>1c</u>	1.57 <sup>c)</sup>	$6.1 \times 10^9$	-38.5

a)  $0.1 \text{ mol dm}^{-3} \text{ Et}_4\text{NClO}_4$  in  $\text{CH}_3\text{CN}$ , platinum electrode, scan rate:  $100 \text{ mV s}^{-1}$ . b) Calculated as  $\tau$  of DCA=11.7 ns.<sup>7</sup> c) Irreversible.

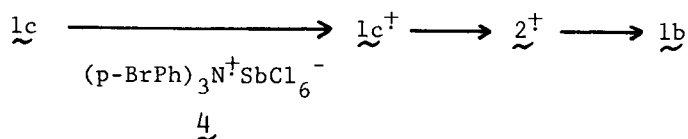
Using these values, free-energy change ( $\Delta G$ ) in the electron transfer from 1a-c to excited 9,10-dicyanoanthracene (DCA) was calculated by the well-known Rehm-Weller equation.<sup>6</sup> These data are summarized in Table 1. The values of  $\Delta G$  indicate that the electron transfer reaction is expected to occur. In fact, the fluorescence of DCA in dichloromethane was quenched by 1a and 1c with rate constants ( $k_q$ ) shown in Table 1.

When a dichloromethane solution of 1a ( $1 \times 10^{-2} \text{ mol dm}^{-3}$ ) containing DCA ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) was irradiated with a 300 W Xenon lamp through Corning 0-51 filter ( $\lambda > 360 \text{ nm}$ ) for 2 h, phenanthrene (40% yield) and trans-stilbene (40% yield) were obtained together with the recovery of 1a (33% yield). Under the same conditions, 1b gave phenanthrene (43% yield) and cis-stilbene (43% yield) with the recovery (57% yield). On the other hand, 1c gave distryl-biphenyl 2 (47% yield) with the recovery (47% yield). These findings show that cyclobutanes 1a and 1b possessing a cis-fused biphenyl skeleton undergo bond cleavage to give phenanthrene and stilbene stereoselectively, whereas in cyclobutane 1c possessing a trans-fused biphenyl skeleton bond cleavage occurs in a different orientation from that of 1a and 1b. These are first examples of electron transfer bond cleavage of cyclobutanes showing orientation selectivities.<sup>8</sup> This result can be rationalized by considering the through-bond interaction between aryl groups which is depicted in Scheme 1 where 3a,b,c correspond to 1a,b,c, respectively. The orientations of the bond cleavage are in agreement with those of the interaction,<sup>9</sup> and thus, the bonds participating in the through-bond interaction are broken. Although the orientation of the interaction in 1a where the phenyl groups interact with the biphenyl group is the same as that in 1b, the former is considered to be larger than the latter because cis-oriented diphenyl groups in 1b can not interact effectively with the biphenyl group due to the steric hindrance between phenyl groups as shown in Scheme 1. The difference of the efficiency of the interaction between 1a and 1b seems to contribute to the difference of oxidation potentials shown in Table 1 and UV spectra between them.<sup>10</sup>



On the other hand, irradiation of a benzene solution of  $\underline{1a}$  containing DCA also resulted in the bond cleavage to give phenanthrene (33% yield) and trans-stilbene (33% yield) with the recovery (67% yield). However, the reaction mechanism in benzene is different from that in dichloromethane. The fluorescence of DCA in benzene was quenched with  $\underline{1a}$  ( $k_{q\tau} = 48 \text{ dm}^3 \text{ mol}^{-1}$ ) and an exciplex emission was observed at 510 nm ( $\lambda_{\text{max}}$ ). The maximum is different from those of the exciplex emission of phenanthrene-DCA ( $\lambda_{\text{max}}$ ; 500 nm) and trans-stilbene ( $\lambda_{\text{max}}$ ; 535 nm). This finding suggests that the reaction occurs diabatically via an exciplex of DCA and cyclobutane  $\underline{1a}$ .<sup>11</sup>

For comparisons with the photochemical reactions mentioned above, the reaction of cyclobutanes  $\underline{1a-c}$  with tris(p-bromophenyl)aminium hexachloroantimonate ( $\underline{4}$ ) which is a useful reagent to produce cation radicals of donors<sup>12</sup> was investigated. Treatment of  $\underline{1a}$  with  $\underline{4}$  (0.1 equiv) in dichloromethane gave phenanthrene (87% yield) and trans-stilbene (87% yield). Under the same conditions,  $\underline{1b}$  did not undergo the bond cleavage reaction and 87% of  $\underline{1b}$  was recovered. This result can be explained in terms of the difference of oxidation potentials.  $\underline{1a}$  with a lower oxidation potentials is more easily oxidized by  $\underline{4}$  to give a cation radical of  $\underline{1a}$  which results in bond cleavage to give phenanthrene and trans-stilbene. On the other hand, surprisingly, the reaction of  $\underline{1c}$  with  $\underline{4}$  gave  $\underline{1b}$  (47% yield) with the recovery (53% yield),<sup>13</sup> suggesting that  $\underline{1b}$  was derived from distyrylbiphenyl  $\underline{2}$  initially formed. In fact, treatment of  $\underline{2}$  with  $\underline{4}$  led to formation of  $\underline{1b}$  (50% yield) together with the recovery (50% yield).<sup>13</sup> The  $(2\pi + 2\pi)$  cyclization of  $\underline{2}$  to  $\underline{1b}$  could not be observed in the DCA-photosensitized reaction of  $\underline{2}$  at all<sup>14</sup> and is characteristic in the aminium salt catalyzed reaction. The mechanism of this novel reaction requiring inversion to cyclize to  $\underline{1b}$  is currently investigated.



### References and Notes

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8. The orientations of the bond cleavage observed here are the same as those in direct irradiation of 1b,c reported by Laarhoven et al.<sup>5</sup> Direct irradiation of 1a with a 300 W Xenon lamp through a pyrex filter gave phenanthrene and stilbene quantitatively. On the other hand, upon irradiation in the absence of DCA with a 300 W Xenon lamp through Corning O-51 filter for 2 h, 1a,b,c were recovered unchanged. The regio-specific cleavages in direct irradiation may be explained in terms of the difference of steric strain as suggested by Laarhoven et al.<sup>5</sup> and Kaupp. G. Kaupp, Angew. Chem. Int. Ed. Engl., 13, 817 (1974).
9. Bond lengths of the cyclobutane bonds calculated by the MMPI method were almost the same. Therefore, the orientations of bond cleavages could not be expected from the bond lengths calculated.
10. 1a;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 277 nm (log $\epsilon$  4.13), 314 (3.57), 1b;  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 274 nm (log $\epsilon$  4.13), 311 (3.56). Although the UV spectra of 1a,b are similar to each other, the absorptions of 1a are a little shifted to longer wavelengths than those of 1b.
11. Recently we have found a novel adiabatic exciplex isomerization. E. Hasegawa, K. Okada, and T. Mukai, J. Am. Chem. Soc., 106, 6852 (1984).
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13. These isomers could not be separated and therefore, the yields were determined by <sup>1</sup>H NMR.
14. Instead, only cis-trans isomerization was observed.

(Received in Japan 19 March 1985)