

Photoinduced Electron-Transfer Reactions of Cage Compounds. Novel Pericyclic Reactions Involving a Chain Process^{†1}

Yoshiro Yamashita,* Hiroshi Ikeda, and Toshio Mukai

Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980, Japan. Received November 14, 1986

Abstract: Photosensitized reactions of cage ketones having a 1,2-diaryl-substituted bicyclo[2.2.0]hexane moiety have been investigated. Although saturated cage ketones **3** were recovered unchanged under the conditions of the photoinduced electron-transfer reactions, cage ketones **4**, which contain a double bond in the bridge, underwent novel pericyclic reactions to give **7** on irradiation in the presence of triphenylpyrylium perchlorate (TPP⁺). Interesting features of this reaction are that the quantum yield for the formation of **7a** is more than unity and the product **7a** acts as a cosensitizer. The proposed reaction mechanism involves a chain process. The mechanism is supported by isolation of an intermediate **9a** which was obtained only when the photoreaction was carried out in the presence of tetramethoxybenzene, which acts as a quencher of the electron-transfer reaction. Addition of salts such as NaClO₄ is effective for suppressing back electron transfer in the DCA-sensitized photoreaction of **4a**.

Recently, much attention has been focused on the photoinduced electron-transfer isomerization.² As to the isomerization between phenylated olefins and cyclobutanes, detailed studies have been done.³ In the cycloreversion of 1,2-diaryl-substituted cyclobutanes, the through-bond interaction between aryl groups has been pointed out to be essential for the occurrence of bond cleavage.^{3j} We have studied the cycloreversion of bishomocubane derivatives **1** possessing diaryl substituents to give dienes **2**⁴ (Chart I). The reaction in a polar solvent such as acetonitrile proceeds via a chain mechanism, while adiabatic exciplex isomerization occurs in benzene or dichloromethane.^{4d} The efficient reactivity is attributed to the strained cyclobutane bond substituted with through-bond interacting diaryl groups as well as a tricyclo[4.2.0.0^{2,5}]octane skeleton favorable for the cycloreversion. However, the electron-transfer reactions of cyclobutanes have been limited to the cycloreversion as described above. The electron-transfer bond cleavage of cyclobutanes produces 1,4-radical cations, which seem to be attractive intermediates to undergo novel reactions. It is of interest to find novel rearrangements of radical cation intermediates since there are relatively few examples of major molecular rearrangements via radical cations.⁵ It is also of significance to study the nature of 1,4-radical cations. If the cycloreversion path is suppressed, it is possible for other reactions to occur. In this connection, the electron-transfer reactions of cage ketones **3** and **4** are interesting for the following reasons. First, they have through-bond interacting diaryl substituents,⁶ which are necessary for the electron-transfer bond cleavage of cyclobutanes. Second, the cyclobutane bond is weakened by strain energy due to the cage structure, which may accelerate reactions from the initially formed 1,4-radical cations. Third, they have a 1,2-diaryl-substituted bicyclo[2.2.0]hexane moiety, which is not suitable for the cycloreversion reaction. From these viewpoints, we have studied the photochemical electron-transfer reactions of cage ketones **3** and **4** and related cage compounds. This paper describes the results involving novel pericyclic rearrangement reactions.

Results and Discussion

Cage ketone **3a** was synthesized by photochemical [2 + 2] cycloaddition of **5**, which was obtained by the addition reaction of a cyclopentadienone derivative with cyclohexadiene.⁷ Cage ketones **4a-c** were synthesized by the similar photoreaction of **6a-c**, which were obtained by the addition reaction of cyclopentadienone derivatives with cycloheptatriene.⁸ Cage ketone **3b** was synthesized by catalytic hydrogenation of **4a**. The oxidation potentials

Chart I

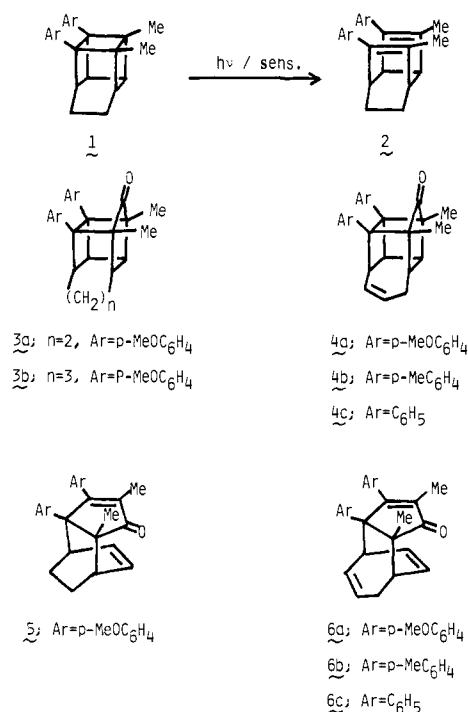


Table I. Oxidation Potentials, Free Energy Changes (ΔG), and TPP⁺ Fluorescence Quenching Data

| compd | $E_{1/2}^{ox}/V$ vs. SCE ^a | $\Delta G/kcal\ mol^{-1}$ | $k_q\tau/M^{-1}\ b$ |
|-----------|---------------------------------------|---------------------------|---------------------|
| 3a | 1.31 ^c | -28.6 | 75 |
| 3b | 1.28 ^c | -29.3 | <i>d</i> |
| 4a | 1.23 ^c | -30.5 | 73 |
| 4c | 1.91 ^c | -14.8 | 56 |

^a0.1 M Et₄NClO₄ in MeCN, platinum electrode, scan rate 100 mV s⁻¹. ^bIn dichloromethane. ^cIrreversible. Calculated as E_{pa} (anodic peak potential) -0.03 V. ^dNo attempt.

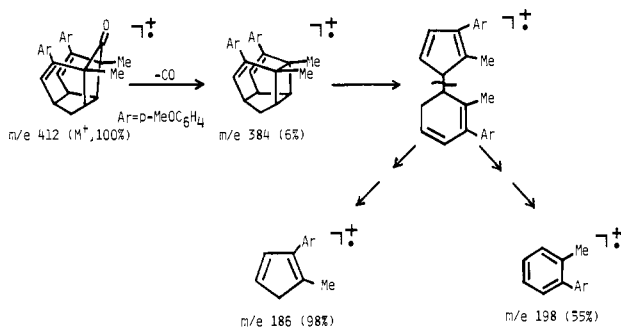
of cage ketones **3** and **4** measured by cyclic voltammetry are shown in Table I. Saturated cage ketones **3a** and **3b** have almost the

(1) Organic Photochemistry, 80. Part 79: Tanaka, N.; Kumagai, T.; Mukai, T. *Tetrahedron Lett.* 1986, 27, 6221.

(2) Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 233-326.

[†]Dedicated to Prof. George Büchi on the occasion of his 65th birthday.

Scheme I



same oxidation potentials, while **4a**, containing a double bond in the bridge, has a little lower oxidation potential than **3a** and **3b**. This difference is attributable to some interaction between the double bond and the cyclobutane bond or the increase of the strain energy due to the incorporation of the double bond. The free energy changes in the photochemical electron-transfer process can be estimated from the Rehm-Weller equation (eq 1),⁹ where $E_{1/2}^{\text{ox}}$

$$\Delta G \text{ (kcal mol}^{-1}\text{)} = 23.06(E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} + C) - \Delta E_{0/0} \quad (1)$$

and $E_{1/2}^{\text{red}}$ are redox potentials of the electron donors and acceptors, respectively. $\Delta E_{0/0}$ is the excitation energy of the sensitizer, and C represents the Coulomb term. The free energy changes (ΔG) in the electron transfer from ketones **3** and **4** to excited 2,4,6-triphenylpyrylium perchlorate (TPP^+) are calculated by eq 1 using $E_{1/2}^{\text{red}}$ (-0.32 V vs SCE in acetonitrile) and $\Delta E_{0/0}$ (66.2 kcal mol⁻¹ in dichloromethane)¹⁰ values for TPP^+ and $E_{1/2}^{\text{ox}}$ values obtained here.¹¹ The values of ΔG shown in Table I are all negative, indicating that the electron transfer is possible. In fact, the fluorescence of TPP^+ was effectively quenched by the ketones with $k_q\tau$ shown in Table I. However, saturated ketones **3a** and **3b** were recovered unchanged under the conditions of photoinduced electron transfer using TPP^+ as sensitizer. *p*-Chloranil or 9,10-dicyanoanthracene (DCA) did not sensitize the reaction at all, although the ΔG values for the electron transfer from ketones **3** to excited sensitizers are large negative.¹²

In contrast, irradiation of a dichloromethane solution¹³ of **4a** with a 300-W xenon lamp through a Corning O-51 filter ($\lambda >$

Table II. Photosensitized Reaction of Cage Ketones **4** Using TPP^+ as Sensitizer^a

| compd | Ar | irrad time/min | rel yield ^b /% | |
|-----------|--|----------------|---------------------------|----------|
| | | | 4 | 7 |
| 4a | <i>p</i> -MeOC ₆ H ₄ | 5 | 0 | 100 |
| 4b | <i>p</i> -MeC ₆ H ₄ | 5 | 62 | 38 |
| 4c | C ₆ H ₅ | 60 | 83 | 17 |

^a [**4**] = 1.3×10^{-2} M, [TPP^+] = 1.9×10^{-3} M in dichloromethane. Irradiation with a 300-W xenon lamp through a Corning O-51 filter ($\lambda > 360$ nm). ^b The relative yields were determined by ¹H NMR analyses.

Table III. Photosensitized Reaction of Cage Ketones **4** Using TPP^+ as Sensitizer in the Presence of TMB^a

| compd | Ar | irrad time/min | rel yield ^b /% | | |
|-----------|--|----------------|---------------------------|----------|----------|
| | | | 4 | 7 | 9 |
| 4a | <i>p</i> -MeOC ₆ H ₄ | 60 | 55 | 24 | 21 |
| 4b | <i>p</i> -MeC ₆ H ₄ | 60 | 93 | 0 | 7 |
| 4c | C ₆ H ₅ | 60 | 93 | 0 | 7 |

^a [**4**] = 1.5×10^{-2} M, [TPP^+] = 1.7×10^{-3} M, [TMB] = 1.6×10^{-2} M in dichloromethane. $\lambda > 360$ nm irradiation. ^b The relative yields were determined by ¹H NMR analyses.

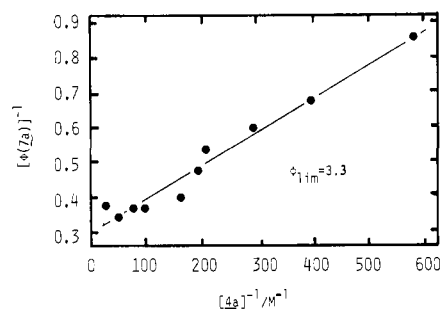
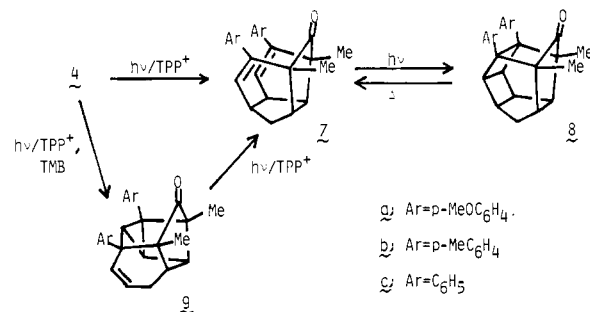


Figure 1. Plots of $[\Phi(7a)]^{-1}$ vs $[4a]^{-1}$. Dichloromethane solution containing TPP^+ (1.5×10^{-4} M). $\lambda = 392 \pm 10$ nm irradiation.

360 nm) under N₂ in the presence of TPP^+ resulted in the quantitative formation of a novel product **7a**. The structure of



7a was determined on the basis of the spectroscopic data along with chemical evidence. The elemental analysis and mass spectrum indicate that **7a** is an isomer of the starting ketone **4a**. The ¹H NMR spectrum strongly supports the structure, in which two olefinic protons appear as doublet peaks. The characteristic coupling pattern can be rationalized by this structure. The structure is also supported by the mass fragmentation pattern shown in Scheme I in which decarbonylation followed by pericyclic bond cleavage occurs. In addition, the fact that irradiation of **7a** quantitatively gave a cage compound **8a** which reverted to **7a** by heating at 70 °C supports the structure.

The following findings suggest that dienone **7a** is formed via a mechanism involving electron transfer. First, dienone **7a** was also produced in 34% yield in the reaction of **4a** with tris(*p*-bromophenyl)aminium hexachloroantimonate, which is a useful reagent to produce radical cations of donors.¹⁴ Second, the photoreaction was sensitive to the substituent effect as shown in

(3) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677. (c) Neunteufl, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (d) Lewis, F. D.; DeVoe, R. J.; MacBlane, D. B. *J. Org. Chem.* **1982**, *47*, 1392. (e) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1386. (f) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1978**, 490. (g) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265. (h) Pac, C.; Fukunaga, T.; Ohtsuki, T.; Sakurai, H. *Chem. Lett.* **1984**, 1847. (i) Yamashita, Y.; Yaegashi, H.; Mukai, T. *Tetrahedron Lett.* **1985**, *26*, 3579. (j) Pac, C. *Pure Appl. Chem.* **1986**, *58*, 1249.

(4) (a) Mukai, T.; Sato, K.; Yamashita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 670. (b) Okada, K.; Hisamitsu, K.; Mukai, T. *Tetrahedron Lett.* **1981**, *22*, 1251. (c) Okada, K.; Hisamitsu, K.; Miyashi, T.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1982**, 974. (d) Hasegawa, E.; Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1984**, *106*, 6852.

(5) Padwa, A.; Chou, C. S.; Rieker, W. F. *J. Org. Chem.* **1980**, *45*, 4555. Roth, H. D.; Schilling, M. L. M.; Gassman, P. G.; Smith, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2711. Gassman, P. G.; Hay, B. A. *Ibid.* **1985**, *107*, 4075. Gassman, P. G.; Hay, B. A. *Ibid.* **1986**, *108*, 4227.

(6) (a) Tezuka, T.; Yamashita, Y.; Mukai, T. *J. Am. Chem. Soc.* **1976**, *98*, 6051. (b) Harano, K.; Ban, T.; Yasuda, M.; Osawa, E.; Kanematsu, K. *J. Am. Chem. Soc.* **1981**, *103*, 2310.

(7) Yamashita, Y.; Mukai, T. *Chem. Lett.* **1978**, 919.

(8) Preparation of **4c** and **6c** has been reported. Houk, K. N.; Woodward, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4143.

(9) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93.

(10) The value was obtained from the absorption and fluorescence spectra.

(11) Since TPP^+ is a cationic sensitizer, the Coulomb term was neglected.

(12) When DCA is used as sensitizer, ΔG values for photoreactions of **3a** and **3b** in dichloromethane are -10.4 and -11.1 kcal mol⁻¹, respectively. When chloranil is used as sensitizer, ΔG values for photoreactions of **3a** and **3b** are -28.3 and -29.0 kcal mol⁻¹. These ΔG values were calculated by using the Coulomb term (+0.16 eV).^{7b}

(13) The reaction also proceeded in acetonitrile. But dichloromethane is a better solvent due to the low solubility of **4a** in acetonitrile as well as the sensitivity of TPP^+ to water.

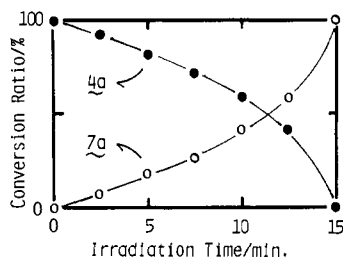


Figure 2. Plots of conversion ratio vs irradiation time. $[4a] = 9.6 \times 10^{-3}$ M, $[TPP^+] = 9.8 \times 10^{-5}$ M. $\lambda > 400$ nm irradiation (filter: Corning 3-74 + Toshiba ND-10). The ratios were determined by ^1H NMR analyses.

Table IV. Photosensitized Reaction of Cage Ketones **4** in the Presence of Cosensitizers^a

| compd | Ar | cosensitizer | irrad time/min | rel yield ^b /% | | |
|-------|---|--------------|----------------|---------------------------|----|-------|
| | | | | 4 | 7 | 9 |
| 4b | <i>p</i> -MeC ₆ H ₄ | pyrene | 5 | 100 | 0 | trace |
| 4b | <i>p</i> -MeC ₆ H ₄ | phenanthrene | 5 | 41 | 59 | 0 |
| 4b | <i>p</i> -MeC ₆ H ₄ | biphenyl | 5 | 46 | 46 | 0 |
| 4c | C ₆ H ₅ | phenanthrene | 60 | 38 | 62 | 0 |
| 4c | C ₆ H ₅ | biphenyl | 60 | 42 | 20 | 0 |

^a $[4] = [\text{cosensitizer}] = 1.3 \times 10^{-2}$ M, $[TPP^+] = 1.9 \times 10^{-3}$ M, in dichloromethane, $\lambda > 360$ nm irradiation. ^b The yields were determined by ^1H NMR analyses.

Table II, which can be rationalized by the oxidation potentials of the ketones; i.e., the lower the oxidation potential, the easier the reaction. Third, the photoreaction took place quantitatively even in the presence of 2,5-di-*tert*-butylpyridine. This fact rules out the possibility that the reaction proceeds by acid catalyst. Furthermore, 1,2,4,5-tetramethoxybenzene (TMB) ($E_{1/2}^{\text{ox}} = 0.81$ V vs SCE) worked as a quencher of the reaction. Thus, irradiation of a dichloromethane solution of **4a** in the presence of TPP⁺ and TMB gave a mixture of **4a**, **7a**, and another product **9a** in the yields shown in Table III. The new product **9a** is an isomer of **4a** and **7a**. The structure was deduced from the ^1H NMR spectrum. The mass spectrum of **9a** is similar to that of **7a** [m/e , 412 (M^+ , 91%), 384 (9%), 199 (66%), 198 (14%), 186 (100%)], suggesting that **9a** easily isomerizes to **7a** by an electron-transfer reaction. In fact, **9a** has a relatively low oxidation potential ($E_{1/2}^{\text{ox}} = 1.25$ V vs SCE) and was quantitatively converted to **7a** by the photosensitized reaction using TPP⁺ as sensitizer. This fact indicates that the rearrangement from **9a**^{•+} to **7a**^{•+} takes place faster than the back electron transfer to give **9a** when TMB does not exist. Similarly, ditolyl derivative **9b** and diphenyl derivative **9c** were identified only in the presence of TMB as shown in Table III.

In order to obtain further evidence for the mechanism of the novel reactions, we have measured the quantum yield of the photoreaction of **4a** to give **7a**. Interestingly, the quantum yield is more than unity and dependent on the concentration of the substrate as shown in Figure 1. The limiting quantum yield is 3.3. This fact suggests the occurrence of a chain reaction.

Another interesting feature is that the rate of reaction increases with the passage of time as shown in Figure 2. In fact, the quantum yield in the presence of the product **7a** is higher than that in the absence of **7a**. Thus, the quantum yield in a dichloromethane solution containing **4a** (9.6×10^{-3} M) and TPP⁺ (9.8×10^{-5} M) is 2.0, while the quantum yield in a dichloromethane solution containing **4a** (4.8×10^{-3} M), **7a** (4.8×10^{-3} M), and TPP⁺ (9.8×10^{-5} M) is 2.9. These facts show that the product **7a** acts as a cosensitizer.¹⁵ In connection with this cosensitization by the product, the effects of additive cosensitizers are of interest. Since the reaction of **4a** is too fast for investigating such effects, the reactions of **4b** and **4c** were investigated. The

(15) The quantum yield in a dichloromethane solution containing **4a** (9.6×10^{-3} M), **7a** (9.6×10^{-3} M), and TPP⁺ (9.8×10^{-5} M) is 3.3. This result shows that the increased quantum yield is not due to the trace impurity acting as a quencher.

Scheme II

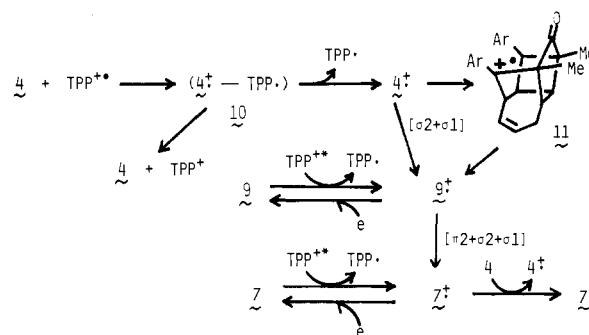


Table V. Photosensitized Reaction of Cage Ketone **4a** Using DCA as Sensitizer in the Presence of Salts^a

| salt | irrad time/min | rel yield ^b /% | | |
|-----------------------------------|----------------|---------------------------|-----|----|
| | | 4a | 7a | 9a |
| | 60 | 100 | 0 | 0 |
| NaClO ₄ | 15 | 0 | 100 | 0 |
| NaClO ₄ ^c | 15 | 100 | 0 | 0 |
| NaI | 65 | 27 | 61 | 13 |
| Et ₄ NClO ₄ | 60 | 92 | 8 | 0 |

^a $[4a] = [\text{salt}] = 1.1 \times 10^{-2}$ M, $[DCA] = 4.1 \times 10^{-4}$ M in MeCN:CH₂Cl₂ (3:2). $\lambda > 360$ nm irradiation. ^b The yields were determined by ^1H NMR analyses. ^c In the presence of 18-crown-6 (1.1×10^{-2} M).

results are summarized in Table IV. Pyrene, whose oxidation potential ($E_{1/2}^{\text{ox}} = 1.15$ V vs SCE¹⁶) is lower than those of **4b** and **4c**, worked as a quencher. On the other hand, phenanthrene, which has a satisfied oxidation potential ($E_{1/2}^{\text{ox}} = 1.58$ V vs SCE¹⁶), sensitizes the reaction a little. In the case of biphenyl ($E_{1/2}^{\text{ox}} = 1.90$ V vs SCE¹⁶), byproducts whose structures have not been determined were obtained along with the products **7b,c**. Such cosensitization is considered to take place via electron transfer from cage ketones **4b,c** to the radical cation of the cosensitizer, which more easily escapes from solvent cage of the geminate radical ion pair as pointed out previously.¹⁷

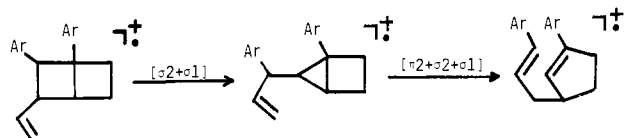
On the basis of these findings, we propose the reaction mechanism shown in Scheme II. Electron transfer from cage compounds **4** to the excited TPP⁺ produces a geminate pair **10**, which gives a solvent-separated radical cation of **4**. A back electron transfer in **10** reproduces **4** and TPP⁺. The poor reactivity of **4b** and **4c** can be attributed to the facile back electron transfer. The solvated **4**^{•+} undergoes a $[\sigma 2 + \sigma 1]$ pericyclic reaction to give **9**^{•+} in which the diaryl-substituted cyclobutane bond is broken. This rearrangement may proceed via an intermediate **11**, which leads to **9**^{•+} by a 1,2-vinyl shift. The formed radical cation **9**^{•+} undergoes a $[\pi 2 + \sigma 2 + \sigma 1]$ pericyclic reaction to give **7**^{•+}. This reaction must be faster than the back electron transfer to give **9** since **9** was not identified at all in the absence of TMB. The chain reaction observed in the reaction of dianisyl derivative **4a** can be explained by considering that electron transfer from **7a**^{•+} to **4a** gives **7a** and the radical cation **4a**^{•+}, which reenters the reaction cycle. This electron-transfer reaction is energetically facilitated since the oxidation potential of **7a** ($E_{1/2}^{\text{ox}} = 1.25$ V vs SCE) is a little higher than that of **4a** ($E_{1/2}^{\text{ox}} = 1.23$ V vs SCE). The acceleration by the product **7a** may be rationalized by considering that the efficiency of escape of **7a**^{•+} from the solvent cage of the geminate pair is larger than that of **4a**^{•+}. The solvated **7a**^{•+} can afford the solvated **4a**^{•+} by exothermic electron transfer.

In the photochemical reactions described above, TPP⁺ was used as sensitizer. Although the reactions also proceeded when *p*-chloranil was used as sensitizer, DCA did not sensitize the reactions at all. In the case of DCA electron transfer from the substrate

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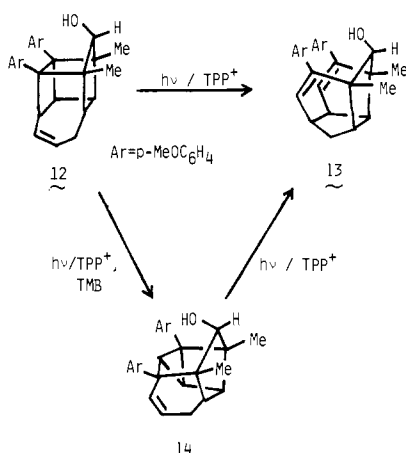
(17) Farid, S.; Hartman, S. E.; Evans, T. R. *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic: New York, 1975; p 327. Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167 and references cited therein.

Scheme III



to excited DCA is also possible since the free energy change (ΔG) in the electron transfer is large negative ($-12.2 \text{ kcal mol}^{-1}$ for **4a**). Even when phenanthrene was added as cosensitizer, no reaction occurred. This result shows that the back electron transfer from $\text{DCA}^{\bullet-}$ takes place more easily than that from $\text{TPP}^{\bullet+}$. Recently, there have been several reports on salt effects describing that some salts are effective in suppressing the back electron transfer.¹⁸ When a few salts were added to a solution of **4a** and DCA in acetonitrile and dichloromethane (3:2), a salt effect was observed as shown in Table V. NaClO_4 is more effective than Et_4NClO_4 , indicating that the salt effect is related to the kind of cation rather than to the kind of anion. Na^+ seems to be better in suppressing the back electron transfer from $\text{DCA}^{\bullet-}$ to the radical cation species by forming a complex. This is supported by the fact that 18-crown-6, which can incorporate Na^+ , quenched the reaction completely as shown in Table V.¹⁹ In the case of NaI , I^- seems to work as a quencher of the radical cation species since **9a**, which was identified only in the presence of a quencher such as TMB, is formed. These results show that it is of great importance to suppress back electron transfer in carrying out photoinduced electron-transfer reactions. In this sense, $\text{TPP}^{\bullet+}$ is a good sensitizer for photochemical electron-transfer reactions.²⁰ It should be also noted that addition of salts provides a powerful method to suppress back electron transfer.

The novel reactions discussed above are the skeletal rearrangements of the 1,2-diaryl-3-vinylbicyclohexane moiety. The ketonic bridge of **4** does not participate directly in the reactions. In order to investigate the effect of the ketonic bridge, the photoinduced electron-transfer reaction of alcohol **12** was investigated.



Alcohol **12**, which was obtained by reduction of **4a**, has a lower oxidation potential ($E_{1/2}^{\text{ox}} = 1.21 \text{ V vs SCE}$) than ketone **4a**. This fact indicates that the ketonic bridge shows some electronic effects

(18) Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *Tetrahedron Lett.* **1985**, 26, 5823. Lewis, F. D.; Petisce, J. R.; Oxman, J. D.; Nepras, M. J. *J. Am. Chem. Soc.* **1985**, 107, 203. Goodman, J. L.; Peters, K. S. *Ibid.* **1986**, 108, 1700. Goodson, B.; Schuster, G. B. *Tetrahedron Lett.* **1986**, 27, 3123 and references cited therein.

(19) Irradiation in the presence of DCA, NaClO_4 , and 2,6-di-*tert*-butylpyridine gave a quantitative yield of **7a**, ruling out the possibility of acid-catalyzed reaction. Irradiation in the presence of only DCA and 18-crown-6 resulted in the complete recovery of **4a**. 18-Crown-6 did not quench the fluorescence of DCA. These findings show that the quenching is caused by the incorporation of Na^+ into 18-crown-6. The effect of crown has been pointed out by Peters et al. Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, 105, 4875.

(20) Recently, triphenylpyrylium salts have been used for photoinduced electron-transfer Diels-Alder reactions. Mattay, J.; Gersdorf, J.; Mertes, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1088. Micoh, J.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 412.

on the diaryl-substituted cyclobutane bond. $\text{TPP}^{\bullet+}$ -photosensitized reaction of **12** gave **13** in 60% yield.²¹ Upon irradiation in the presence of TMB, an isomer **14** was isolated which isomerized to **13** by the photosensitized reaction using $\text{TPP}^{\bullet+}$. The fact that alcohol **12** underwent the same rearrangements as ketones **4** indicates that only the 1,2-vinylbicyclohexane moiety is essential for the occurrence of the novel pericyclic reactions. Scheme III depicts the skeletal rearrangements which are new types of pericyclic reactions of radical cations. The first reaction requires only the 1,2-diaryl-3-vinylcyclobutane moiety. We are continuing to study the photoinduced electron-transfer reactions of 1,2-diaryl-3-vinylcyclobutane derivatives to investigate the generality of the novel reactions found here.

Experimental Section

General Methods. IR spectra were taken on a Shimadzu IR-27G spectrometer and UV spectra on a Hitachi 340 spectrophotometer. Mass data were collected on a Hitachi M-52 mass spectrometer. ^1H NMR spectra were obtained at 90 MHz on a Varian EM-390 or at 200 MHz on a Varian XL-200 spectrometer. ^{13}C NMR spectra were obtained at 50 MHz on a Varian XL-200 spectrometer or at 22.49 MHz on a Jeol FX-90Q spectrometer. Redox potentials were measured on a Yanako P-1000 voltammeter. Liquid chromatographic analyses were performed on a Shimadzu LC-6A liquid chromatograph equipped with a Shimadzu C-R3A Chromatopac. Preparative thin-layer chromatography was performed on 0.5 mm \times 20 cm \times 20 cm silica gel (E. Merck 60PF₂₅₄) plates. Wako Q-22 silica gel was used for column chromatography. Dichloromethane was distilled from calcium hydride. All melting points are uncorrected.

Preparation of Trienone 6a. A solution of 11.5 g (18.0 mmol) of 2,5-dimethyl-3,4-bis(4-methoxyphenyl)cyclopentadienone dimer and 5.7 mL (55 mmol) of cycloheptatriene in 80 mL of toluene was heated at reflux under nitrogen for 87 h. Evaporation of the solvent gave orange crystals, which were washed with ether followed by recrystallization from dichloromethane-ethanol to give 4.55 g (31% yield) of **6a** as colorless crystals: mp 206–207 °C; IR (KBr) 1675 cm^{-1} ; ^1H NMR (CDCl_3 , 90 MHz) δ 0.93 (s, 3 H), 1.81 (s, 3 H), 2.09 (m, 1 H), 2.41 (m, 1 H), 2.54 (dddd, 1 H, $J = 18.0, 3.8, 3.8, 0.8 \text{ Hz}$), 2.86 (ddd, 1 H, $J = 7.5, 5.3, 1.8 \text{ Hz}$), 3.73 (s, 3 H), 3.81 (s, 3 H), 5.33 (ddd, 1 H, $J = 10.9, 3.8, 3.8 \text{ Hz}$), 5.73–6.20 (m, 3 H), 6.43–6.90 (m, 6 H), 7.06–7.30 (m, 2 H).

Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{O}_3$: C, 81.52; H, 6.84. Found: C, 81.53; H, 6.84.

Preparation of Trienone 6b. A solution of 12.6 g (22 mmol) of 2,5-dimethyl-3,4-bis(4-methylphenyl)cyclopentadienone dimer and 7.0 mL (67 mmol) of cycloheptatriene in 100 mL of toluene was heated at reflux under nitrogen for 96 h. The red oil obtained after removal of the solvent was chromatographed on a silica gel column. Elution with chloroform-carbon tetrachloride gave yellow crystals, which were recrystallized from dichloromethane-ethanol to give 6.4 g (38% yield) of **6b** as colorless cubes: mp 200–200.5 °C; IR (KBr) 1680 cm^{-1} ; ^1H NMR (CDCl_3 , 90 MHz) δ 0.98 (s, 3 H), 1.79 (s, 3 H), 2.08 (m, 1 H), 2.28 (s, 3 H), 2.37 (s, 3 H), 2.41 (m, 1 H), 2.52 (dddd, 1 H, $J = 18.0, 4.0, 4.0, 1.5 \text{ Hz}$), 2.84 (ddd, 1 H, $J = 9.0, 6.0, 2.0 \text{ Hz}$), 5.31 (ddd, 1 H, $J = 10.5, 4.0, 3.0 \text{ Hz}$), 5.73–6.21 (m, 3 H), 6.36–6.55 (m, 2 H), 6.87–7.20 (m, 6 H).

Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{O}$: C, 88.38; H, 7.42. Found: C, 88.56; H, 7.66.

Preparation of Cage Ketone 4a. A solution of 3.83 g (9.27 mmol) of **6a** in 1 L of dichloromethane was irradiated through a Pyrex filter with Rayonet RUL-3500 Å lamps under nitrogen bubbling for 5 h. Removal of the solvent gave a yellow oil, which was crystallized from ethanol to give 3.66 g (96% yield) of **4a**. Recrystallization from dichloromethane-ethanol gave **4a** as colorless prisms: mp 179.5–180 °C; IR (KBr) 1740 cm^{-1} ; mass spectrum (25 eV), m/e (relative intensity) 413 ($\text{M}^+ + 1$, 22), 412 (M^+ , 68), 385 (21), 384 (68), 369 (16), 303 (17), 199 (70), 187 (17), 186 (100), 185 (67); ^1H NMR (CDCl_3 , 90 MHz) δ 0.92 (s, 3 H), 1.10 (s, 3 H), 2.07 (dd, 1 H, $J = 8.3, 3.8 \text{ Hz}$), 2.65 (m, 2 H), 2.82 (dd, 1 H, $J = 7.0, 3.8 \text{ Hz}$), 3.27 (ddd, 1 H, $J = 7.5, 5.3, 1.5 \text{ Hz}$), 3.65 (s, 6 H), 3.87 (dd, 1 H, $J = 7.0, 3.9 \text{ Hz}$), 5.60 (m, 1 H), 5.82 (dddd, 1 H, $J = 11.5, 7.5, 1.5, 1.5 \text{ Hz}$), 6.50–6.82 (m, 8 H).

Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{O}_3$: C, 81.52; H, 6.84. Found: C, 81.57; H, 6.95.

Preparation of Cage Ketone 4b. A solution of 5.0 g (13 mmol) of **6b** in 2 L of MeOH-benzene was irradiated through a Pyrex filter under nitrogen with Rayonet RUL-3500 Å lamps for 4 h. Removal of the

(21) The rate of the isomerization of **12** was slower than that of **4a**. The difference may be attributed to the difference in the strain energy between **12** and **4a**.

solvent followed by crystallization from ethanol gave 4.9 g (98% yield) of **4b**, which was recrystallized from dichloromethane-ethanol to give **4b** as colorless cubes: mp 144–145 °C; IR (KBr) 1740 cm⁻¹; mass spectrum (25 eV), *m/e* (relative intensity) 380 (M⁺, 7), 352 (6), 184 (19), 183 (37), 171 (17), 170 (100), 169 (14); ¹H NMR (CDCl₃, 90 MHz) δ 0.91 (s, 3 H), 1.12 (s, 3 H), 2.06 (dd, 1 H, *J* = 8.3, 3.8 Hz), 2.14 (s, 6 H), 2.65 (m, 2 H), 2.83 (dd, 1 H, *J* = 6.5, 3.8 Hz), 3.31 (ddd, 1 H, *J* = 6.8, 5.4, 1.5 Hz), 3.90 (dd, 1 H, *J* = 6.5, 5.4 Hz), 5.66 (dd, 1 H, *J* = 11.0, 1.5 Hz), 5.80 (dddd, 1 H, *J* = 11.0, 6.8, 1.5, 1.5 Hz), 6.63–6.97 (m, 8 H).

Anal. Calcd for C₂₈H₂₈O: C, 88.38; H, 7.42. Found: C, 88.39; H, 7.42.

Preparation of Cage Ketone 3b. In a hydrogenation apparatus, 220 mg (0.533 mmol) of **4a** was hydrogenated in 25 mL of acetic acid with 20 mg of 5% Pd-C. Removal of the solvent followed by recrystallization from ethanol gave 210 mg (95% yield) of **3b** as colorless crystals: mp 156–157 °C; IR (KBr) 1740 cm⁻¹; ¹H NMR (CDCl₃, 90 MHz) δ 0.92 (s, 3 H), 1.08 (s, 3 H), 1.56–1.99 (m, 6 H), 2.08 (m, 1 H), 2.66 (dd, 1 H, *J* = 6.8, 3.8 Hz), 3.33 (m, 1 H), 3.44 (dd, 1 H, *J* = 6.8, 5.3 Hz), 3.63 (s, 6 H), 6.48–6.87 (m, 8 H).

Anal. Calcd for C₂₈H₃₀O₃: C, 81.12; H, 7.29. Found: C, 80.89; H, 7.21.

Preparation of Cage Alcohol 12. To a solution of 1.21 g (2.9 mmol) of cage ketone **4a** in 100 mL of tetrahydrofuran, 260 mg of LiAlH₄ (7.0 mmol) was added under nitrogen. After the solution was refluxed for 44 h under nitrogen, the usual workup followed by recrystallization from ether-*n*-hexane gave 830 mg (69% yield) of **12** as colorless crystals: mp 156.5–157.5 °C; IR (KBr) 3525 cm⁻¹; ¹H NMR (CDCl₃, 90 MHz) δ 0.88 (s, 3 H), 1.19 (s, 3 H), 1.87 (dd, 1 H, *J* = 7.5, 4.5 Hz), 1.89 (br s, 1 H), 2.50 (dd, 1 H, *J* = 6.9, 4.5 Hz), 2.60 (m, 2 H, *J* = 7.5, 1.5, 1.5 Hz), 2.87 (ddd, 1 H, *J* = 7.8, 5.7, 1.0 Hz), 3.49 (s, 1 H), 3.53 (dd, 1 H, *J* = 6.9, 5.7 Hz), 3.64 (s, 3 H), 3.70 (s, 3 H), 5.62 (m, 1 H), 5.83 (dddd, 1 H, *J* = 10.5, 7.8, 1.5, 1.5 Hz), 6.43–6.80 (m, 4 H), 7.12–7.30 (m, 4 H); ¹³C NMR (CDCl₃, 50 MHz) δ 14.06 (q), 14.80 (q), 31.76 (t), 41.86 (d), 43.58 (d), 44.96 (d), 47.19 (d), 51.78 (s), 54.89 (q), 55.02 (q), 55.27 (s), 62.90 (s), 70.59 (s), 90.99 (d), 112.21 (d, 2 C), 112.98 (d, 2 C), 129.46 (d), 129.61 (d, 2 C), 129.69 (d, 2 C), 130.77 (s), 131.39 (d), 137.28 (s), 156.87 (s), 157.59 (s).

Anal. Calcd for C₂₈H₃₀O₃: C, 81.13; H, 7.29. Found: C, 81.14; H, 7.52.

TPP⁺-Sensitized Irradiation of Cage Ketone 4a. A mixture of **4a** (26.8 mg, 6.5 × 10⁻⁵ mol) and TPP⁺ (3.9 mg, 9.5 × 10⁻⁶ mol) in 5 mL of N₂-purged dichloromethane was irradiated through a Corning O-51 filter with a 300-W xenon lamp for 5 min. Removal of the solvent followed by thin-layer chromatography (3:2 *n*-hexane-ether) gave colorless crystals (27.0 mg, 100% yield) of **7a**. Recrystallization from dichloromethane-ethanol gave **7a** as colorless plates: mp 135–136 °C; IR (KBr) 3000–2850, 1715, 1605, 1510, 1240, 1030, 825 cm⁻¹; UV (CH₂Cl₂) 236 nm sh (log ε 4.17), 253 (4.15), 270 sh (4.12); ¹H NMR (CDCl₃, 200 MHz) δ 1.02 (s, 3 H), 1.27 (s, 3 H), 1.89 (d, 1 H, *J* = 11.5 Hz), 2.02 (ddd, 1 H, *J* = 11.5, 4.0, 3.5 Hz), 2.41 (dd, 1 H, *J* = 7.0, 4.0 Hz), 3.03 (dd, 1 H, *J* = 10.0, 7.0 Hz), 3.10 (ddd, 1 H, *J* = 8.0, 6.0, 3.5 Hz), 3.75 (s, 3 H), 3.81 (s, 3 H), 3.86 (ddd, 1 H, *J* = 10.0, 6.0, 3.0 Hz), 5.57 (d, 1 H, *J* = 8.0 Hz), 5.68 (d, 1 H, *J* = 3.0 Hz), 6.68–6.97 (m, 6 H), 7.53–7.57 (m, 2 H); ¹³C NMR (CDCl₃, 50 MHz) δ 21.12 (q), 23.35 (q), 34.56 (t), 40.21 (d), 44.55 (d), 55.11 (q), 55.18 (q), 57.08 (s), 58.69 (d), 58.75 (d), 60.16 (s), 112.94 (d, 2 C), 113.53 (d, 2 C), 128.47 (d, 2 C), 128.69 (s), 129.81 (d, 2 C), 131.92 (d), 133.50 (s), 137.16 (d), 140.09 (s), 149.53 (s), 158.39 (s), 158.71 (s), 221.38 (s).

Anal. Calcd for C₂₈H₂₈O₃: C, 81.52; H, 6.84. Found: C, 81.53; H, 6.97.

TPP⁺-Sensitized Irradiation of Cage Ketone 4a in the Presence of TMB. A mixture of **4a** (31.0 mg, 7.5 × 10⁻⁵ mol), TPP⁺ (3.4 mg, 8.3 × 10⁻⁶ mol), and TMB (15.6 mg, 7.9 × 10⁻⁵ mol) in 5 mL of dichloromethane was irradiated for 1 h under the same conditions as those in the absence of TMB. Removal of the solvent gave a mixture whose ¹H NMR spectrum showed the relative yields of **4a**:**7a**:**9a** to be 55:24:21. Thin-layer chromatography (3:2 *n*-hexane-ether) afforded recovered **4a** (14.4 mg, 47% yield), **7a** (7.1 mg, 23% yield), and **9a** (7.0 mg, 23% yield). Recrystallization from dichloromethane-ethanol gave **9a** as colorless needles: mp 167.5–168.5 °C; IR (KBr) 3025–2825, 1730, 1610, 1512, 1240, 1155, 1025, 820 cm⁻¹; UV (CH₂Cl₂) 235 nm (log ε 4.14), 273 (3.52), 280 (3.51); ¹H NMR (CDCl₃, 200 MHz) δ 0.64 (s, 3 H), 1.21 (s, 3 H), 1.30 (dd, 1 H, *J* = 6.8, 1.2 Hz), 1.73 (dd, 1 H, *J* = 6.5, 6.0 Hz), 2.24 (br dd, 1 H, *J* = 18.0, 3.0 Hz), 2.45 (dddd, 1 H, *J* = 18.0, 6.5, 3.0, 1.5 Hz), 2.56 (ddd, 1 H, *J* = 6.0, 5.0, 1.2 Hz), 2.61 (dd, 1 H, *J* = 6.8, 5.0 Hz), 3.73 (s, 3 H), 3.83 (s, 3 H), 6.02 (dd, 1 H, *J* = 10.5, 1.5 Hz), 6.08 (ddd, 1 H, *J* = 10.5, 3.0, 3.0 Hz), 6.76–7.22 (m, 8 H); ¹³C NMR (CDCl₃, 22.49 MHz) δ 14.03 (q), 14.88 (q), 20.69 (d), 24.61 (t), 37.01 (d), 40.86 (d), 41.19 (d), 45.17 (d), 46.28 (s), 51.18 (s), 52.74 (s), 55.16

(q, 2 C), 112.86 (d, 2 C), 113.84 (d, 2 C), 126.18 (d), 127.35 (d, 2 C), 129.51 (d, 2 C), 129.70 (s), 133.23 (d), 135.58 (s), 157.90 (s), 158.10 (s), 221.08 (s).

Anal. Calcd for C₂₈H₂₈O₃: C, 81.52; H, 6.84. Found: C, 81.75; H, 7.01.

TPP⁺-Sensitized Irradiation of Ketone 9a. A mixture of **9a** (15.0 mg, 3.6 × 10⁻⁵ mol) and TPP⁺ (4.2 mg, 1.0 × 10⁻⁵ mol) in dichloromethane (5 mL) was irradiated for 1 h under the same conditions as those for **4a**. The NMR spectrum of the residue obtained by removal of the solvent showed a quantitative formation of **7a**.

TPP⁺-Sensitized Irradiation of Cage Ketone 4b in the Presence of TMB. A mixture of **4b** (85.8 mg, 2.3 × 10⁻⁴ mol), TPP⁺ (10.2 mg, 2.5 × 10⁻⁵ mol), and TMB (234 mg, 1.18 × 10⁻³ mol) in 15 mL of N₂-purged dichloromethane was irradiated through a Toshiba L-39 filter (λ > 360 nm) with a 2-kW xenon lamp for 9 h. Removal of the solvent followed by thin-layer chromatography gave recovered **4b** (11 mg, 13% yield), **7b** (8 mg, 9% yield), and **9b** (37 mg, 43% yield). **7b**: mp 166–167 °C (from dichloromethane-ethanol); IR (KBr) 3050–2850, 1720, 1505, 1440, 995, 820, 790, 520 cm⁻¹; UV (CH₂Cl₂) 228 nm (log ε 4.22), 246 (4.14), 268 sh (4.06); mass spectrum (25 eV), *m/e* (relative intensity) 380 (M⁺, 12), 183 (31), 172 (7), 169 (100); ¹H NMR (CDCl₃, 90 MHz) δ 1.06 (s, 3 H), 1.26 (s, 3 H), 1.88 (d, 1 H, *J* = 10.8 Hz), 2.00 (ddd, 1 H, *J* = 10.8, 3.8, 3.5 Hz), 2.23 (s, 3 H), 2.30 (s, 3 H), 2.37 (dd, 1 H, *J* = 7.2, 3.8 Hz), 3.00 (dd, 1 H, *J* = 9.8, 7.2 Hz), 3.05 (ddd, 1 H, *J* = 7.5, 6.0, 3.5 Hz), 3.80 (ddd, 1 H, *J* = 9.8, 6.0, 3.0 Hz), 5.51 (d, 1 H, *J* = 7.5 Hz), 5.67 (d, 1 H, *J* = 3.0 Hz), 6.77–7.12 (m, 6 H), 7.32–7.52 (m, 2 H).

Anal. Calcd for C₂₈H₂₈O: C, 88.38; H, 7.42. Found: C, 88.41; H, 7.42.

9b: mp 155–156 °C (dichloromethane-ethanol); IR (KBr) 3010–2800, 1730, 1515, 1450, 1425, 1370, 1025, 810 cm⁻¹; UV (CH₂Cl₂) 234 nm (log ε 4.10), 272 (3.09), 281 sh (2.82); mass spectrum (25 eV), *m/e* (relative intensity) 380 (M⁺, 11), 183 (62), 171 (8), 170 (100); ¹H NMR (CDCl₃, 90 MHz) δ 0.63 (s, 3 H), 1.22 (s, 3 H), 1.32 (dd, 1 H, *J* = 6.3, 1.6 Hz), 1.70 (ddd, 1 H, *J* = 6.0, 6.0, 1.5 Hz), 2.27 (s, 3 H), 2.33 (s, 3 H), 2.05–2.57 (m, 3 H), 2.61 (dd, 1 H, *J* = 6.3, 4.5 Hz), 5.08 (d, 1 H, *J* = 10.5 Hz), 6.03 (d, 1 H, *J* = 10.5 Hz), 6.85–7.17 (m, 8 H).

Anal. Calcd for C₂₈H₂₈O: C, 88.38; H, 7.42. Found: C, 88.22; H, 7.51.

TPP⁺-Sensitized Irradiation of Cage Ketone 4c in the Presence of TMB. A mixture of **4c** (79.7 mg, 2.3 × 10⁻⁴ mol), TPP⁺ (10.2 mg, 2.5 × 10⁻⁵ mol), and TMB (234 mg, 1.18 × 10⁻³ mol) in 15 mL of N₂-purged dichloromethane was irradiated through a Toshiba L-39 filter (λ > 360 nm) with a 2-kW xenon lamp for 9 h. Removal of the solvent followed by thin-layer chromatography gave recovered **4c** (10 mg, 12% yield), **7c** (11 mg, 14% yield), and **9c** (41 mg, 51% yield). **7c**: mp 96–97 °C (from dichloromethane-ethanol); IR (KBr) 3050–2850, 1725, 1490, 1450, 1370, 995, 985, 965, 885, 760, 705, 695 cm⁻¹; UV (CH₂Cl₂) 242 nm (log ε 4.08), 264 sh (4.00); mass spectrum (25 eV), *m/e* (relative intensity) 353 (M⁺ + 1, 10), 352 (M⁺, 40), 169 (47), 156 (100); ¹H NMR (CDCl₃, 90 MHz) δ 1.07 (s, 3 H), 1.28 (s, 3 H), 1.90 (dd, 1 H, *J* = 11.0, 1.5 Hz), 2.03 (dd, 1 H, *J* = 11.0, 4.0 Hz), 2.40 (m, 1 H), 3.03 (dd, 1 H, *J* = 9.8, 7.0 Hz), 3.08 (ddd, 1 H, *J* = 8.0, 6.0, 1.5 Hz), 3.85 (ddd, 1 H, *J* = 9.8, 6.0, 3.0 Hz), 5.57 (d, 1 H, *J* = 8.0 Hz), 5.73 (d, 1 H, *J* = 3.0 Hz), 6.82–7.33 (m, 8 H), 7.48–7.60 (m, 2 H).

Anal. Calcd for C₂₆H₂₄O: C, 88.60; H, 6.86. Found: C, 88.49; H, 6.89.

9c: mp 168–169 °C (from dichloromethane-ethanol); IR (KBr) 3050–2800, 1730, 1600, 1490, 1445, 1425, 1370, 1050, 755, 730, 700, 670 cm⁻¹; UV (CH₂Cl₂) 236 nm (log ε 4.00), 262 (3.09), 272 sh (2.80); mass spectrum (25 eV), *m/e* (relative intensity) 352 (M⁺, 8), 170 (7), 169 (69), 156 (100); ¹H NMR (CDCl₃, 90 MHz) δ 0.63 (s, 3 H), 1.23 (s, 3 H), 1.38 (dd, 1 H, *J* = 6.2, 1.2 Hz), 1.72 (ddd, 1 H, *J* = 6.0, 6.0, 1.8 Hz), 2.07–2.62 (m, 3 H), 2.67 (dd, 1 H, *J* = 6.2, 4.5 Hz), 6.00 (d, 1 H, *J* = 10.8 Hz), 6.04 (d, 1 H, *J* = 10.8 Hz), 6.93–7.37 (m, 10 H).

Anal. Calcd for C₂₆H₂₄O: C, 88.60; H, 6.86. Found: C, 88.43; H, 6.80.

TPP⁺-Sensitized Irradiation of Cage Alcohol 12. A mixture of **12** (26.9 mg, 6.5 × 10⁻⁵ mol) and TPP⁺ (3.9 mg, 9.5 × 10⁻⁶ mol) in 5 mL of N₂-purged dichloromethane was irradiated through a Corning O-51 filter with 300-W xenon lamp for 10 min. Removal of the solvent followed by thin-layer chromatography (9:1 *n*-hexane-ether) gave colorless crystals (16.2 mg, 60% yield) of **13**, which was recrystallized from ether-*n*-hexane as colorless crystals: mp 104–105 °C; IR (neat) 3550, 3050, 2800, 1605, 1510, 1460, 1450, 1285, 1180, 1150, 835–820 cm⁻¹; UV (CH₂Cl₂) 236 nm (log ε 4.15), 271 (4.07); mass spectrum (25 eV), *m/e* (relative intensity) 415 (M⁺ + 1, 29), 414 (M⁺, 100), 201 (10), 199 (55), 198 (21), 187 (41), 186 (79), 185 (14), 135 (10), 121 (14), 108 (10); ¹H NMR (CDCl₃, 90 MHz) δ 1.28 (br s, 1 H), 1.30 (s, 3 H), 1.48 (s, 3 H), 1.75 (m, 2 H), 2.15 (m, 1 H), 2.60 (dd, 1 H, *J* = 9.8, 6.8 Hz), 2.75 (m, 1 H), 3.43 (ddd, 1 H, *J* = 9.8, 6.0, 3.0 Hz), 3.55 (br s, 1 H), 3.70 (s, 3

H), 3.78 (s, 3 H), 5.58 (d, 1 H, $J = 7.5$ Hz), 5.87 (d, 1 H, $J = 3.0$ Hz), 6.52-7.07 (m, 6 H), 7.53-7.70 (m, 2 H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 26.43 (q), 29.94 (q), 34.58 (t), 40.37 (d), 47.70 (d), 51.55 (s), 55.11 (q, 2 C), 56.91 (d), 57.54 (s), 60.52 (d), 90.85 (d), 113.14 (d, 2 C), 113.33 (d, 2 C), 129.64 (d, 2 C), 129.85 (s), 130.46 (d, 2 C), 131.87 (d), 136.48 (s), 136.85 (d), 140.53 (s), 146.72 (s), 158.13 (s), 158.46 (s).

Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{O}_3$: C, 81.13; H, 7.29. Found: C, 81.01; H, 7.53.

TPP⁺-Sensitized Irradiation of Cage Alcohol 12 in the Presence of TMB. A mixture of **12** (31.1 mg, 7.5×10^{-5} mol), TPP⁺ (3.5 mg, 8.6×10^{-6} mol), and TMB (15.9 mg, 8.0×10^{-5} mol) in 5 mL of dichloromethane was irradiated for 1 h under the same conditions as those in the absence of TMB. Thin-layer chromatography (9:1 *n*-hexane-ether) gave recovered **12** (12.3 mg, 40% yield) and **14** (17.3 mg, 56% yield), which was recrystallized from ethanol: mp 129.5-130 °C; IR (KBr) 3600-3300, 3000-2800, 1505, 1240, 1230, 1175, 1165, 1040, 835 cm^{-1} ; UV (CH_2Cl_2) 231 nm ($\log \epsilon$ 4.36), 280 (3.51); mass spectrum (25 eV), m/e (relative intensity) 415 ($\text{M}^+ + 1$, 24), 414 (M^+ , 100), 322 (19), 201 (19), 200 (25), 199 (93), 198 (19), 188 (13), 187 (77), 186 (93), 185 (19), 135 (12), 121 (26), 108 (21); ^1H NMR (CDCl_3 , 200 MHz) δ 0.99 (s, 3 H), 1.23 (s, 3 H), 1.30 (dd, 1 H, $J = 7.0, 6.0$ Hz), 1.38 (dd, 1 H, $J = 6.5, 0.5$ Hz), 1.59 (br d, 1 H, $J = 6.0$ Hz), 2.09 (ddd, 1 H, $J = 6.0, 4.5, 0.5$ Hz), 2.11 (ddd, 1 H, $J = 19.0, 3.4, 2.0$ Hz), 2.33 (dd, 1 H, $J = 6.5, 4.5$ Hz), 2.36 (dddd, 1 H, $J = 19.0, 7.0, 3.4, 2.0$ Hz), 2.94 (d, 1 H, $J = 6.0$ Hz), 3.79 (s, 3 H), 3.85 (s, 3 H), 5.69 (ddd, 1 H, $J = 10.0, 2.0, 2.0$ Hz), 5.86 (ddd, 1 H, $J = 10.0, 3.4, 3.4$ Hz), 6.77-6.97 (m, 4 H), 7.22-7.37 (m, 4 H); ^{13}C NMR (CDCl_3 , 22.49 MHz) δ 19.39 (d), 20.50 (q, 2 C), 24.94 (t), 37.86 (d), 40.08 (s), 42.17 (d), 42.56 (d), 42.82 (s), 44.19 (s, 2 C), 55.16 (q, 2 C), 84.27 (d), 113.19 (d, 2 C), 113.65 (d, 2 C), 125.07 (d), 128.01 (d, 2 C), 130.82 (d, 2 C), 132.12 (s), 136.95 (d), 138.91 (s), 157.58 (s), 157.90 (s).

Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{O}_3$: C, 81.13; H, 7.29. Found: C, 80.84; H, 7.57.

Direct Irradiation of Ketone 7a. A solution of 634 mg (1.54 mmol) of **7a** in 400 mL of dichloromethane was irradiated through a Pyrex filter with Rayonet RUL-3500 Å lamps under nitrogen bubbling for 90 min. Removal of the solvent followed by recrystallization from dichloromethane-ethanol gave 524 mg (83% yield) of **8** as colorless crystals: mp 121-122 °C; IR (KBr) 2950, 2850, 1750, 1610, 1515, 1465, 1280, 1240, 1175, 1025, 825 cm^{-1} ; UV (CH_2Cl_2) 237 nm ($\log \epsilon$ 4.18), 278 (3.47), 286 (3.40); mass spectrum (25 eV), m/e (relative intensity) 413 ($\text{M}^+ + 1$, 23), 412 (M^+ , 72), 384 (6), 200 (11), 199 (64), 198 (6), 187 (15), 186 (100); ^1H NMR (CDCl_3 , 200 MHz) δ 0.60 (s, 3 H), 1.26 (s, 3 H), 1.52 (ddd, 1 H, $J = 12.5, 2.0, 1.5$ Hz), 1.59 (ddd, 1 H, $J = 12.5, 5.0, 3.5$ Hz), 2.48 (ddd, 1 H, $J = 8.0, 5.0, 1.5$ Hz), 2.96 (dd, 1 H, $J = 8.0, 8.0$ Hz), 3.34 (dddd, 1 H, $J = 5.0, 5.0, 3.5, 2.0$ Hz), 3.42 (ddd, 1 H, $J = 8.0, 5.0, 3.0$ Hz), 3.50 (dd, 1 H, $J = 3.0, 3.0$ Hz), 3.53 (dd, 1 H, $J = 5.0, 3.0$ Hz), 3.65 (s, 3 H), 3.70 (s, 3 H), 6.27-6.50 (m, 6 H), 6.92-7.00 (m, 2 H).

Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{O}_3$: C, 81.52; H, 6.84. Found: C, 81.50; H, 7.06.

TPP⁺ Fluorescence Quenching. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrophotometer. The quenching experiments were carried out in air by monitoring the changes in the intensity at 464 nm of fluorescence as a function of concentration of quencher. The slope of I^0/I vs [quencher], which equals $k_q\tau$, was determined by a least-squares method.

Quantum Yield Determinations. Samples were irradiated with a Ushio 150-W xenon lamp on a Hitachi MPF-4 spectrometer ($\lambda_{\text{ex}} = 392 \pm 10$ nm). The number of photons incident on the sample were determined by using a potassium ferrioxalate actinometer. The formation of **7a** was followed by liquid chromatography (column, Merck silica 150; solvent, 95:5 *n*-hexane-ethyl acetate; flow rate, 1.0 mL/min).

Nucleophilic Attacks on Carbon-Carbon Double Bonds. 34.^{1,2} Intramolecular Element Effect in Competitive Expulsion of Two Halide Nucleofuges as a Tool for Investigating the Rapid Step of Nucleophilic Vinylic Substitution

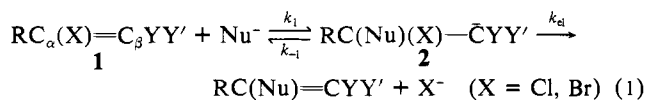
Bianca Avramovitch,^{3a} Peter Weyerstahl,^{3b} and Zvi Rappoport^{*3a}

Contribution from the Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel, and the Institut für Organische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, West Germany. Received January 21, 1987

Abstract: The substitution of 9-(bromochloromethylene)fluorene (**8**) and β,β -bis(*p*-nitrophenyl)- α -bromo- α -chloroethylene (**9**) by *p*-toluenethiolate and *p*-cresolate ions gives the monobromo, the monochloro, and the disubstitution products. The [monochloro]/[monobromo] substitution product ratios were determined in CD_3CN , $\text{DMSO}-d_6$, and $\text{DMSO}-d_6$ - CD_3OD under conditions where the disubstitution was negligible. The ratios were 2.0-3.2, were slightly higher for **8** than for **9**, and showed no discernible solvent dependence. The ratios did not change in the presence of radical traps although an ESR spectrum was observed with **8** and *p*- $\text{MeC}_6\text{H}_4\text{S}^-$. The "intermolecular element effects" $k_{\text{Br}}/k_{\text{Cl}}$ derived from competitive substitution of **8** or **9** with their dibromo or dichloro analogues were 1.2-1.76. The results were interpreted in terms of a multistep nucleophilic vinylic substitution proceeding via an intermediate carbanion, which may be formed either directly or by an initial single-electron transfer followed by combination of the anion radical and the radical. The ratios of the products were hence identified as the ratios of the rate constants for expulsion of Br^- and Cl^- ($k_{\text{el}}(\text{Br})/k_{\text{el}}(\text{Cl})$)—the "intramolecular element effect" from the carbanion. The low ratios and their relative insensitivity to the solvent and to the delocalizing ability of negative charge of the β -substituents were ascribed to an early transition state for the expulsion of halide ions from the carbanion. Generalizations concerning the expulsion of poor and good nucleofuges from carbanions substituted by poor and good electron-withdrawing groups are discussed.

Recent accumulating evidence⁴⁻⁶ on the mechanism of bimolecular nucleophilic vinylic substitution,⁷ which involves a rate-

determining nucleophilic attack on C_α where C_β carries two electron-withdrawing groups Y and Y' (eq 1), suggests that the



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(2) For a preliminary report, see: Avramovitch, B.; Rappoport, Z. 51st Annual Meeting of the Israel Chemical Society, Oct 9-10, 1985, Haifa, Abstract p 56 (O1).

(3) (a) The Hebrew University. (b) Technischen Universität Berlin.

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