

Substitution Effects on Regioselective Cyclizations of 1,5- and 2,4-Diphenyl-1,5-hexadiene Cation Radicals Generated by the Electron-Transfer Photosensitizations

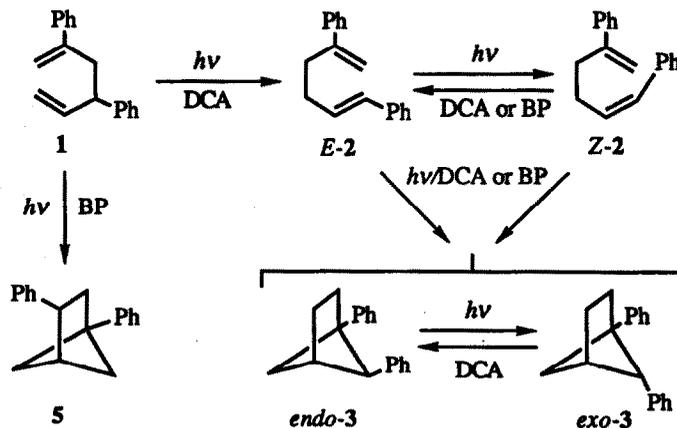
Hiroshi Ikeda,[†] Tomo Oikawa, and Tsutomu Miyashi*

College of General Education[†] and Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Abstract: The 9,10-Dicyanoanthracene (DCA)-sensitized electron-transfer photoreactions of *E*- and *Z*-1,5-diphenyl-1,5-hexadienes (*E*-2 and *Z*-2) gave a mixture of *endo*- and *exo*-1,5-diphenylbicyclo[2.1.1]hexanes (*endo*-3 and *exo*-3) while 2,4-diphenyl-1,5-hexadiene (1) underwent the Cope rearrangement to *E*-2, showing significant substitution effects on cyclization of 1,5-hexadiene cation radicals.

We previously reported that the photosensitized electron-transfer (PET) reactions of 2,5-diaryl-1,5-hexadienes provided the unprecedented Cope rearrangement which was accompanied by the formation of the bicyclo[2.2.0]hexane system in a photostationary mixture.¹ The important key step in those stereospecific PET Cope rearrangements was the initial cyclization of 2,5-diaryl-1,5-hexadiene cation radicals to 1,4-diaryl-cyclohexa-1,4-diyl cation radicals in which charge and spin are directly stabilized by two aryl groups. It was thus assumed that a change of an aryl substitution in the 1,5-hexadiene skeleton may induce a different type of reaction. In order to gain insight into substitution effects on cyclization of 1,5-hexadiene cation radicals, we examined the PET reactions of 1², *E*-2² and *Z*-2^{2,3} under the DCA-sensitized conditions. We found that similar to the 2,5-diphenyl substitution the 2,4-diphenyl substitution involved the Cope rearrangement, while 1,5-diphenylbicyclo[2.1.1]hexanes were formed by the 1,5-diphenyl substitution (Scheme 1).

Scheme 1



As shown in Table 1, oxidation potentials ($E^{ox}_{1/2}$)^a of 1, *E*-2 and *Z*-2 were low enough to quench the excited singlet state of DCA exothermically. In accord with the calculated free energy changes (ΔG)⁵, the DCA fluorescence was quenched by 1 and 2 efficiently in CH₃CN and also in less polar CH₂Cl₂ and C₆H₆, albeit less efficiently. Upon irradiation ($\lambda > 360$ nm)⁶ of a CD₂Cl₂ solution of 1 and DCA at 20 °C, a mixture of *endo*-3³ and *exo*-3³ was formed

together with *E*-2 as shown in Table 2. Similar results were obtained in CD₃CN, but in C₆D₆ a trace amount of *Z*-2 was formed together with *E*-2, *endo*-3 and *exo*-3. Time-dependent change of product ratios monitored by ¹H-NMR in CD₂Cl₂ revealed that at the early stage the relative yield of *E*-2 slowly increased up to 12 % in maximum and then decreased along with the steady formation of *endo*-3 and *exo*-3. Those results suggest that 1 irreversibly rearranged to *E*-2 which, in turn, formed *endo*-3 and *exo*-3. In fact, similar PET reactions of *E*-2 gave rise to *endo*-3 and *exo*-3 and the isomerization to *Z*-2 was concurrent in C₆D₆. Similarly, a mixture of *endo*-3 and *exo*-3 was formed from *Z*-2 as shown in Table 2. It is of interest to note that the *endo*-3/*exo*-3 ratio significantly increased upon prolonged irradiation and reached a photostationary state. The independent PET reactions of *endo*-3 and *exo*-3 confirmed the *endo*-*exo* isomerization and a photostationary ratio changed from 87:13 in CD₃CN to 95:5 and >99:<1, respectively, in CD₂Cl₂ and C₆D₆.

A plausible electron-transfer mechanism taking all those observations into account is shown in Scheme 2. The initially formed 1⁺⁺ preferentially cyclizes to *eC*-4⁺⁺ rather than to *aC*-4⁺⁺ and 8⁺⁺, through which the Cope rearrangement to *E*-2 occurs. Because *d*₂-1⁷ gave only *d*₂-*E*-2 but not *d*₂-*E*-2' at all and any deuterium scrambling was not observed in the recovered *d*₂-1, an alternative stepwise pathway through 6⁺⁺ does not operate in the PET Cope rearrangement of 1. The fact that the 1,3-diphenyl isomer 5³ was afforded quantitatively by the benzophenone (BP)-sensitized photoreaction of 1 but was not formed in the DCA-sensitized photoreaction also eliminates a possible operation of a triplet mechanism through 31^{*}. The thermodynamic stability of *eC*-4⁺⁺ relative to *aC*-4⁺⁺ and 8⁺⁺ is one of key factors for 1⁺⁺ to cyclize preferentially to *eC*-4⁺⁺.

In contrast, a major process involved by the 1,5-diphenyl substitution is cyclization of 2⁺⁺ to 7⁺⁺ stabilized directly by two phenyl groups. The successive closure then forms a mixture of *endo*-3 and *exo*-3. Because the *endo*-*exo* isomerization was scarcely observed in the BP-sensitized photoreactions of *endo*-3 and *exo*-3,

Table 1. Oxidation Potentials, Free Energy Changes, and Quenching Rate Constants for ¹DCA^{*} of 1, 2, and 3.

	$E^{ox}_{1/2}$ ^{a)}	ΔG	k_q ^{b)/10¹⁰M⁻¹s⁻¹}		
	V	kcal/mol	CH ₃ CN	CH ₂ Cl ₂	C ₆ H ₆
1	+1.79	-3.9	0.74	0.050	0.008
<i>E</i> -2	+1.59	-8.5	1.5	0.83	0.13
<i>Z</i> -2	+1.69	-6.2	1.4	0.15	0.010
<i>endo</i> -3	+1.89	-1.6	0.20	0.038	0.004
<i>exo</i> -3	+1.76	-4.6	0.79	0.32	0.059

a) vs. SCE in CH₃CN. b) Calculated from the Stern-Volmer constants ($k_q\tau$).

Table 2. The DCA-Sensitized Photoreactions of 1, 2, and 3 in CD₃CN, CD₂Cl₂, and C₆D₆.

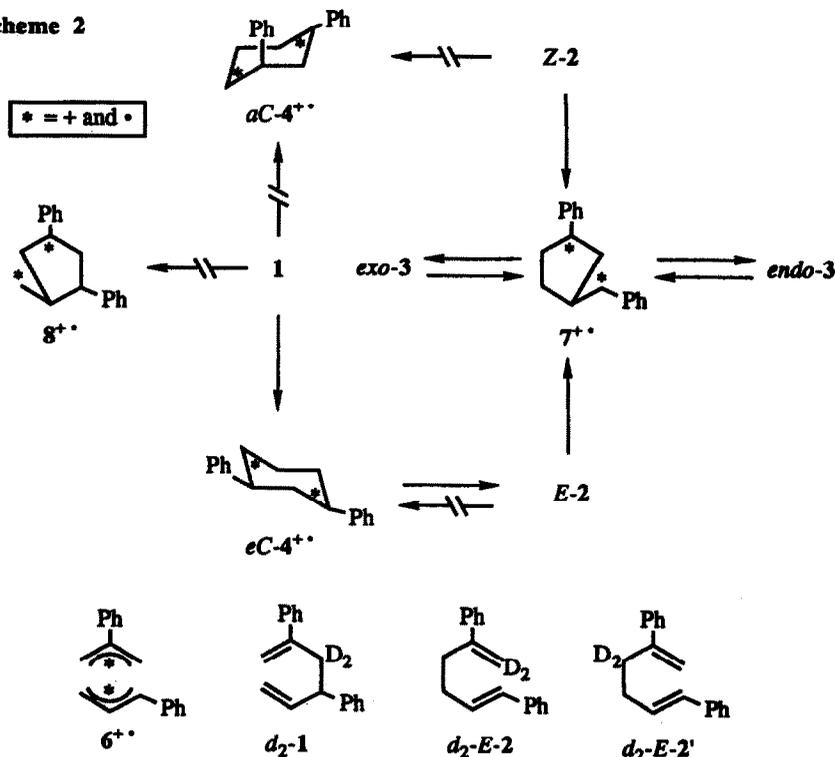
	CD ₃ CN						CD ₂ Cl ₂						C ₆ D ₆					
	Time	Yields ^{a)/%}					Time	Yields ^{a)/%}					Time	Yields ^{a)/%}				
		h	1	<i>E</i> -2	<i>Z</i> -2	<i>endo</i> -3		<i>exo</i> -3	h	1	<i>E</i> -2	<i>Z</i> -2		<i>endo</i> -3	<i>exo</i> -3	h	1	<i>E</i> -2
1	5	44	21	0	10	7	2	8	2	0	63	2	5	55	4	1	14	1
<i>E</i> -2	2	0	80	0	5	3	1	0	6	0	71	3	1	0	55	7	37	1
<i>Z</i> -2	2	0	0	88	8	4	0.5	0	0	2	94	4	1	0	3	68	29	<1
<i>endo</i> -3	2	0	0	0	87	13	1	0	0	0	92	4	2	0	0	0	>99	<1
<i>exo</i> -3	10	0	0	0	76	12	1	0	0	0	85	4	2	0	0	0	>99	<1

a) Yields were determined by ¹H-NMR analyses using an internal standard.

the solvent-dependent change of a photostationary ratio can be mainly ascribed to significant differences in the rate constants (k_q) for DCA-fluorescence quenching between *endo*-3 and *exo*-3 as shown in Table 1. In the PET reactions, a triplet mechanism through $^3\text{2}^*$ might operate in nonpolar C_6D_6 because the *E-Z* isomerization between *E*-2 and *Z*-2 was concurrent. In fact, the BP ($E_T=69$ kcal/mol)-sensitized photoreactions of *E*-2 and *Z*-2 in C_6D_6 gave a mixture of *endo*-3 and *exo*-3 (83:17) accompanying the *E-Z* isomerization. Under the PET conditions, $^3\text{2}^*$ might be efficiently generated by the back electron transfer from DCA^- to 2^+ because the triplet energies⁸ of *E*-2 (ca. 60 kcal/mol) and *Z*-2 (ca. 62 kcal/mol) are comparable with the ion pair energies of [*E*- 2^{2+} /DCA $^-$] (59 kcal/mol) and [*Z*- 2^{2+} /DCA $^-$] (61 kcal/mol), respectively. However, the triplet mechanism does not operate in the more polar CD_3CN and CD_2Cl_2 because the *E-Z* isomerization was not concurrent. This was confirmed by the fact that *E*-2 efficiently afforded *endo*-3 and *exo*-3 without the *E-Z* isomerization in the 2,6,9,10-tetracyanoanthracene (TECA)-sensitized photoreactions which can not produce $^3\text{E-2}^*$ energetically.⁹

The cation radical cyclizations of 1^{+} and 2^{+} can be initiated by an intramolecular charge-transfer interaction between a neutral olefin unit as an electron donor and an olefin cation radical unit as an electron acceptor. Therefore, observed regioselective cyclizations can be reasonably accounted for by differences in the orbital coefficients of the HOMO for two olefin units in 1 and 2 which also correlate with those of the SOMO for an olefin cation radical unit.¹⁰ Similar to 2,5-diphenyl-1,5-hexadiene, 1 has the larger orbital coefficients of the HOMO at C-1 and C-6 than at C-2 and C-5, respectively. However, the orbital coefficients of the HOMO of 2 at C-2 and C-6 are larger than those at C-1 and C-5. Consequently, cyclization of 1^{+} occurs at C-1 and C-6, whereas 2^{+} at C-2 and C-6 no matter which olefin unit is oxidized to a cation radical. The results shown here

Scheme 2



thus revealed the importance of phenyl substitution effects for regioselective intramolecular cyclizations of 1,5-hexadiene cation radicals.

This paper was dedicated to professor H. Hart on the occasion of his 70th birthday (TM). We thank financial supports from the Ministry of Education, Science and Culture (Grant-in-Aid for Scientific Research Nos., 03303001, 03403005, and 04740284).

REFERENCES AND NOTES

- (a) Miyashi, T.; Konno, A.; Takahashi, Y. *J. Am. Chem. Soc.*, **1988**, *110*, 3676-3677. (b) Miyashi, T.; Ikeda, H.; Konno, A.; Okitsu, O.; Takahashi, Y. *Pure Appl. Chem.*, **1990**, *62*, 1531-1538. (c) Miyashi, T.; Takahashi, Y.; Ohaku, H.; Ikeda, H.; Morishima, S. *ibid.*, **1991**, *63*, 223-230.
- Dienes **1** and **E-2** were obtained according to the published procedure.^{2a} Diene **Z-2** was synthesized by the Wittig reaction of **Z-1,5-diphenyl-4-penten-1-one**.^{2b} (a) Dewar, M. J. S.; Wade, Jr., L. E. *J. Am. Chem. Soc.*, **1977**, *99*, 4417-4424. (b) Cowan, D. O.; Baum, A. A. *ibid.*, **1971**, *93*, 1153-1162.
- Satisfactory elemental analyses were obtained for all new compounds in this report. **Z-2**: Colorless oil, bp 100 °C / 0.2 mmHg. MS (*m/z*, %): 235(M⁺+1, 4), 234(M⁺, 28), 143(100), 142(28), 118(28). ¹H-NMR (200 MHz, CDCl₃): δ_{ppm} 2.50(td, 2H, 7.3, 6.8), 2.63(t, 2H, 7.3), 5.07(s, 1H), 5.30(s, 1H), 5.69(dt, 1H, 11.8, 6.8), 6.42(d, 1H, 11.8), 7.12-7.46(m, 10H). ¹³C-NMR (50 MHz, CDCl₃): δ_{ppm} 27.29, 35.43, 112.62, 126.13(2C), 126.49, 127.35, 128.10(2C), 128.26(2C), 128.68(2C), 129.32, 131.87, 137.59, 141.15, 147.75. **endo-3**: Colorless oil. MS (*m/z*, %): 235(M⁺+1, 5), 234(M⁺, 17), 143(100), 142(13). ¹H-NMR (400 MHz, CDCl₃): δ_{ppm} 1.43(d, 1H, 6.5), 1.63(m, 1H), 1.73(m, 1H), 1.77(dddd, 1H, 11.0, 9.0, 4.0, 2.5), 1.84(dddd, 1H, 6.5, 3.0, 2.5, 2.5), 1.91(dddd, 1H, 11.0, 9.0, 4.0, 1.5), 2.92(dddd, 1H, 3.0, 3.0, 1.5, 1.5), 3.31(br s, 1H), 6.93(m, 2H), 7.12-7.23(m, 3H), 7.27(m, 1H), 7.38(m, 2H), 7.47(m, 2H). ¹³C-NMR (50 MHz, CDCl₃): δ_{ppm} 25.40, 26.43, 39.03, 43.88, 53.75, 56.78, 125.67, 126.21, 127.13(2C), 127.41(2C), 127.94(2C), 128.26(2C), 140.69, 142.87. **exo-3**: Colorless columns, mp 72.5 °C. MS (*m/z*, %): 235(M⁺+1, 4), 234(M⁺, 10), 143(100). ¹H-NMR (400 MHz, CDCl₃): δ_{ppm} 1.52(dd, 1H, 7.0, 7.0), 1.88-2.04(m, 3H), 2.32(m, 1H), 2.50(dddd, 1H, 7.0, 3.0, 2.5, 2.5), 2.85(ddd, 1H, 3.0, 1.5, 1.5), 3.13(d, 1H, 7.0), 6.95(m, 2H), 7.05-7.27(m, 8H). ¹³C-NMR (50 MHz, CDCl₃): δ_{ppm} 27.87, 35.77, 37.65, 40.30, 56.98, 59.71, 125.52, 125.97, 126.88(2C), 127.56(2C), 127.87(2C), 129.06(2C), 139.37, 142.03. **5**: Colorless oil, bp 100 °C / 0.05 mmHg. MS (*m/z*, %): 234(M⁺, 10), 143(50), 142(10), 130(14), 118(11), 117(100), 115(29). ¹H-NMR (200 MHz, CDCl₃): δ_{ppm} 1.68-1.82(m, 3H), 1.97(m, 1H), 2.04(ddd, 1H, 10.8, 4.0, 2.8), 2.41(ddd, 1H, 10.8, 9.0, 1.8), 2.82(ddd, 1H, 2.6, 2.6, 1.4), 3.55(ddd, 1H, 9.0, 4.0, 1.4), 7.14-7.37(m, 10H). ¹³C-NMR (50 MHz, CDCl₃): δ_{ppm} 39.91, 40.58, 40.91, 44.43, 45.17, 54.26, 125.59, 125.78(2C), 126.01, 127.47(2C), 128.16(2C), 128.23(2C), 143.96, 145.24.
- Redox potentials were measured by cyclic voltammetry at a platinum electrode in dry CH₃CN with 0.1 M Et₄NClO₄ as a supporting electrode. Halfwave oxidation potentials (*E*_{ox1/2}) were estimated as *E*_{pa} (anodic peak potentials) - 0.03 V.
- Free energy changes (Δ*G*) were estimated by the following equation^{5a,b}: Δ*G* = 23.06[*E*_{ox1/2}(sub.) - *E*_{red1/2}(DCA) - *E*₀₋₀] - *e*²/*εr*, where *E*_{red1/2}(DCA) is -0.95 V vs. SCE, *E*₀₋₀ is 2.91 eV, and the coulomb term (*e*²/*εr*) is ignored after Farid's example.^{5c} (a) Rehm, D.; Weller, A. *Isr. J. Chem.*, **1970**, *8*, 259-271. (b) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93-98. (c) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.*, **1990**, *112*, 4290-4301.
- A 0.5 mL solution was irradiated with a 2 kW xenon lamp through a Toshiba cutoff filter L-39 at 20 °C under nitrogen atmosphere.
- Labeled **d**₂-**1** (98 % D incorporation) was obtained by deuteration^{7a} of 1,3-diphenyl-4-penten-1-one followed by the Wittig reaction. (a) Shiner, Jr., V. J.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.*, **1968**, *90*, 418-426.
- Triplet energies of **E-2** and **Z-2** were estimated from those of α-methylstyrene (62.2 kcal/mol), *trans*-β-methylstyrene (59.6 kcal/mol), and *cis*-β-methylstyrene (65.7 kcal/mol).^{8a} (a) Crosby, P. M.; Dyke, J. M.; Metcalfe, J.; Rest, A. J.; Salisbury, K.; Sodeau, J. R. *J. Chem. Soc., Perkin Trans.*, **2**, **1977**, 182-185.
- On the basis of redox potentials of **E-2** and TECA (*E*_{red1/2} = -0.45 V), the free energy change (Δ*G*) for the formation of ³**E-2*** from ion pair (**E-2**⁺/TECA⁻) was estimated to be endothermic by ca. 13 kcal/mol.
- Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley and Sons, Inc.: London, **1976**; pp. 33-85 and pp. 182-207.