



1,3-Bis(4-methoxyphenyl)cyclohexane-1,3-diyl cation radical: divergent reactivity depending upon electron-transfer conditions

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Abstract—1,3-Bis(4-methoxyphenyl)cyclohexane-1,3-diyl cation radical gives 1,5-bis(4-methoxyphenyl)bicyclo[3.1.0]hexane through 1,3-bis(4-methoxyphenyl)cyclohexane-1,3-diyl when generated by photoinduced electron transfer, but gives 4,4'-dimethoxy-*m*-terphenyl when generated by using one-electron oxidant, demonstrating its divergent reactivity depending upon the electron-transfer conditions employed. © 2001 Elsevier Science Ltd. All rights reserved.

We previously reported that 1,4-diphenylcyclohexane-1,4-diyl cation radical (**2**^{•+}, Scheme 1) generated from 2,5-diphenylhexa-1,5-diene (**1**) under the 9,10-dicyanoanthracene (DCA)-sensitized electron-transfer conditions does not undergo cleavage to 2,5-diphenylhexa-1,5-diene cation radical (**1**^{•+}), but suffers back electron transfer (BET) to form 1,4-diphenylcyclohexane-1,4-diyl (**2**), through which cleavage takes place to complete the degenerate Cope rearrangement of **1**.¹ In contrast, one-electron oxidation reactions of **1** and 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (**3**) by cerium(IV) ammonium nitrate (CAN) result in the formation of *p*-terphenyl (**4**) via **2**^{•+} and 1,4-diphenylcyclohex-1-en-4-yl in a successive deprotonation–oxidation mechanism.^{1–3} The observed striking contrast between photoinduced electron-transfer and one-electron oxidant-catalyzed

reactions prompted us to investigate the generation and reactivity of 1,3-diarylcyclohexane-1,3-diyl cation radical. We studied electrontransfer reactions of 1,5-bis(4-

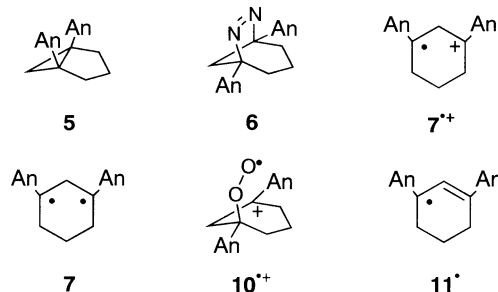
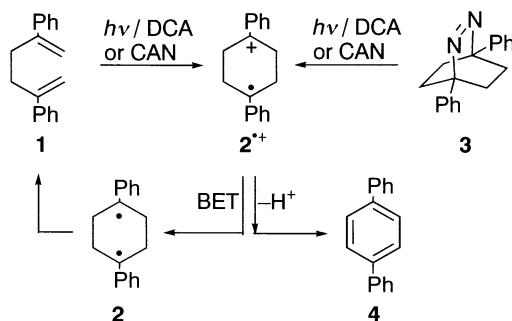


Figure 1. An = 4-MeOC₆H₄.



Scheme 1.

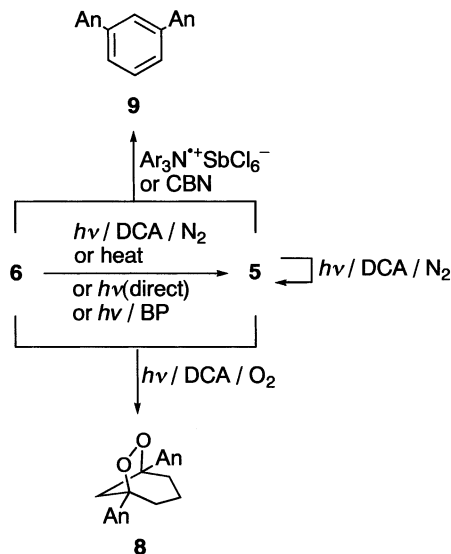
Keywords: photochemistry; cation radical; back electron transfer; electron transfer; reaction mechanism.

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† Satisfactory elemental microanalyses were obtained for all new compounds in this report. Selected data for **5**, **6**, and **8** were as follows. **5**: mp 92–93°C (colorless leaves from EtOH); ¹H NMR (200 MHz, CDCl₃) δ 1.24–1.50 (m, 3H), 1.79 (m, 1H), 2.05–2.37 (m, 4H), 3.72 (s, 6H), 6.69 (AA'BB', *J* = 8.8 Hz, 4H), 6.98 (d, *J* = 8.8 Hz, 4H); ¹³C NMR (50 MHz, CDCl₃) δ 18.2, 20.5, 35.9 (2C), 38.5 (2C), 55.1 (2C), 113.3 (4C), 129.4 (4C), 134.2 (2C), 157.4 (2C); MS *m/z* 294 (100, M⁺), 263 (22), 235 (24), 121 (26). **6**: dp 99–100°C (colorless needles from CH₂Cl₂-*n*-hexane); UV (CH₂Cl₂) λ_{max} (N=N) 350 nm; ¹H NMR (200 MHz, CDCl₃) δ 1.23 (m, 1H), 1.70 (m, 3H), 1.95 (m, 4H), 3.83 (s, 6H), 6.96 (AA'XX', *J* = 8.6 Hz, 4H), 7.52 (AA'XX', *J* = 8.6 Hz, 4H); ¹³C NMR (50 MHz, CDCl₃) δ 19.9, 29.5 (2C), 47.8, 55.3 (2C), 91.6 (2C), 114.0 (4C), 127.1 (4C), 135.3 (2C), 159.0 (2C); MS *m/z* 294 (100, M⁺-N₂), 263 (22), 235 (22), 121 (30). **8**: dp 150–151°C (colorless needles from EtOH); ¹H NMR (200 MHz, CDCl₃) δ 1.94–2.24 (m, 5H), 2.48 (m, 1H), 2.75 (d, *J* = 11 Hz, 1H), 2.88 (broad d, *J* = 11 Hz, 1H), 3.80 (s, 6H), 6.88 (AA'XX', *J* = 9.0 Hz, 4H), 7.35 (AA'XX', *J* = 9.0 Hz, 4H); ¹³C NMR (50 MHz, CDCl₃) δ 19.9, 36.2 (2C), 55.2 (2C), 58.0, 87.2 (2C), 113.8 (4C), 126.8 (4C), 133.0 (2C), 159.2 (2C); MS *m/z* 326 (100, M⁺), 294 (62, M⁺-O₂), 293 (77), 177 (82), 135 (100).

methoxyphenyl)bicyclo-[3.1.0]hexane (**5**, Fig. 1)[†] and 1,5-bis(4-methoxyphenyl)-6,7-diazabicyclo[3.2.1]oct-6-ene (**6**)[†] under various electron-transfer conditions and found that it is also the case with the reactivity of 1,3-bis(4-methoxyphenyl)cyclohexane-1,3-diyl cation radical (**7**^{•+}).

Diazene **6** was prepared by the BF₃·Et₂O-catalyzed reaction⁴ of 1,5-bis(4-methoxyphenyl)hex-5-en-1-one tosylhydrazone. Bicyclohexane **5** was obtained quantitatively by pyrolysis, direct irradiation, and benzophenone (BP)-sensitized photoreaction of **6**. The halfwave oxidation potentials ($E^{\text{ox}}_{1/2}$)[‡] of **5** (+0.77 V versus SCE in acetonitrile) and **6** (+1.28 V) are low enough to quench the excited singlet state of DCA exergonically, as suggested by the calculated free energy change for electron transfer,[§] $\Delta G_{\text{et}} = -1.19$ and -0.68 eV in acetonitrile, respectively. In agreement with the calculation, **5** and **6** quench the fluorescence of DCA efficiently with rate constants, $k_q = 1.7$, 1.6 , and $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for **5**, and 1.4 , 1.1 , and $0.84 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for **6**, respectively, in aerated acetonitrile, dichloromethane, and benzene. In spite of large k_q close to the diffusion control rate, the DCA-sensitized photoreactions of **5** ($\lambda > 360 \text{ nm}$) under nitrogen in acetonitrile, dichloromethane, or benzene result in a quantitative recovery, but 1,5-bis(4-methoxyphenyl)-6,7-dioxabicyclo[3.2.1]octane (**8**, Scheme 2)[†] is efficiently formed under oxygen in polar acetonitrile and dichloromethane (Table 1). Similar irradiation ($\lambda > 410 \text{ nm}$) of DCA with **6** under nitrogen affords **5** quantitatively in acetonitrile, dichloromethane, and benzene. Deazetation of **6** also occurs quantitatively under oxygen, giving rise to **5** together



Scheme 2.

[†] The values of $E^{\text{ox}}_{1/2}$ were estimated as E_{pa} (anodic peak potentials) -0.03 V , which were measured by cyclic voltammetry at a platinum electrode in dry acetonitrile with $0.1 \text{ M Et}_4\text{N}^+\text{ClO}_4^-$ as a supporting electrolyte.

[§] The values of ΔG_{et} were estimated by using the Rehm–Weller equation:⁵ $\Delta G_{\text{et}} (\text{eV}) = E^{\text{ox}}_{1/2} (\text{sub}) - E^{\text{red}}_{1/2} (\text{DCA}) - E_{0-0} (\text{DCA}) - e^2/\epsilon r$, where $E^{\text{red}}_{1/2} (\text{DCA}) = -0.95 \text{ V}$ and $E_{0-0} (\text{DCA}) = 2.91 \text{ eV}$ in acetonitrile and the coulombic term ($e^2/\epsilon r$) is disregarded.⁶

with **8** as a minor product. Of course, prolonged irradiation of **6** gives **8** quantitatively under oxygen.

Interestingly, one-electron oxidation reactions of **5** and **6** by tris(4-bromophenyl)aminium hexachloroantimonate ($\text{Ar}_3\text{N}^+\text{SbCl}_6^-$) give rapidly 4,4'-dimethoxy-*m*-terphenyl (**9**) under nitrogen and even under oxygen. As shown in Table 1, the cerium(IV) tetra-*n*-butylammonium nitrate [$\text{Ce}(n\text{-Bu}_4\text{N})_2(\text{NO}_2)_6$, CBN]⁷⁻-catalyzed reaction of **5** and **6** under nitrogen forms **9** similarly but slowly. Under oxygen, CBN-catalyzed reaction gives **9** together with **8** as a minor product.

Scheme 3 shows plausible mechanistic connections among all reactions. The DCA-sensitized photoreactions of **5** and **6** initially form cation radicals **5**^{•+} and **6**^{•+}, which undergo cleavage and deazetation, respectively, to form **7**^{•+}. Then, a facile BET from DCA^{•-} to **7**^{•+} succeeds to form diyl **7** under nitrogen and oxygen. The inertness of **5** under nitrogen is likely due to the degeneracy of **5**. The degeneracy of **5** and formation of **5** from **6** are completed by cyclization of **7**. The fact that pyrolysis, direct irradiation, or BP-sensitized photoreaction of **6** forms **5** supplements the intervention of **7** in the DCA-sensitized photoreactions of **5** and **6**. Under oxygen, however, relatively slow oxygenation of **7**^{•+} competes with BET, forming **8** through **10**^{•+}.[†] On the other hand, one-electron oxidant-catalyzed reactions of **5** and **6** similarly form **7**^{•+}, but BET to form **7** is energetically unfavorable under these one-electron oxidation conditions. Thus, cation radical **7**^{•+} formed from **5** and **6** then gives rise to **9** under nitrogen and a mixture of **8** and **9** through **11**^{•+} under oxygen, as shown in Scheme 3.

Time-resolved absorption spectroscopy upon laser flash photolysis (LFP)^{||} and γ -ray irradiation^{**} directly observed cation radicals derived from **5** and **6**. Under *N*-methylquinolinium tetrafluoroborate ($\text{NMQ}^+\text{BF}_4^-$)-toluene-cosensitized conditions in dichloromethane, nanosecond LFP of **5** and **6** exhibit nearly the same spectra with an intense absorption band with λ_{max} at 565 nm together with a weak band at 495 nm, as shown in Fig. 2.^{††} These results suggest that **5**^{•+} and **6**^{•+} afford the same transient species. It is noteworthy that upon

[†] The fact that the DCA-sensitized reaction of **5** slowly afforded **8** even in nonpolar benzene (Table 1) suggests that molecular oxygen capture of **7** may occur concurrently (Scheme 3).

^{||} Nanosecond absorption spectroscopy upon LFP was carried out with a pulsed Xe arc lamp (150 W) and a XeCl excimer laser (Lumonics EX600, $\lambda_{\text{ex}} = 308 \text{ nm}$, 100 mJ) at the Advanced Instrumental Laboratory for Graduate Research of Department of Chemistry, Graduate School of Science, Tohoku University.

^{**} A sample solution (10 mM) was degassed by repeating five freeze (77 K)–pump (10^{-3} mmHg)–thaw (ambient temperature) cycles and sealed at 10^{-3} mmHg at 77 K. This matrix was irradiated at 77 K for 8 h with γ -ray from a 5.1 TBq ⁶⁰Co source at the Cobalt 60 γ Ray Irradiation Facility, Tohoku University.

^{††} Similarly, absorption bands with λ_{max} at 549 and 485 nm were observed by LFP (Continuum Surelite-10 YAG laser, Nd, THG, $\lambda_{\text{ex}} = 355 \text{ nm}$, 55 mJ) of **5** in acetonitrile under the DCA–biphenyl-cosensitized conditions.

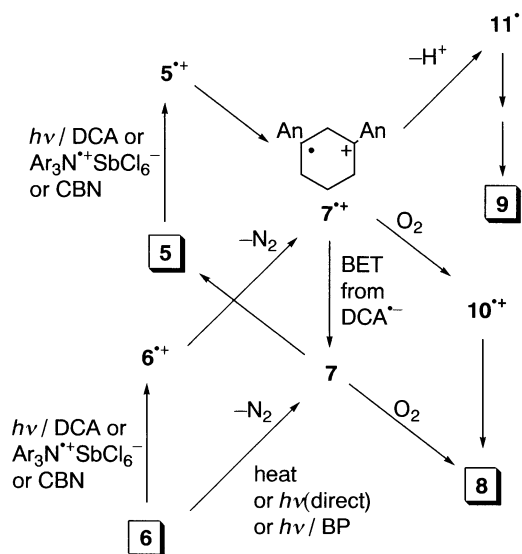
Table 1. Electron-transfer reactions of **5** and **6** under various conditions

Conditions	5				6				
	Time (h)	Conv. (%)	Yields ^a (%)		Time (h)	Conv. (%)	Yields ^a (%)		
			8	9			5	8	9
<i>hν</i> /DCA/CH ₃ CN/N ₂ ^b	0.33	0	–	0	1	54	54	–	0
<i>hν</i> /DCA/CH ₂ Cl ₂ /N ₂ ^b	2	0	–	0	1	100	100	–	0
<i>hν</i> /DCA/C ₆ H ₆ /N ₂ ^b	2	0	–	0	1	96	96	–	0
<i>hν</i> /DCA/CH ₃ CN/O ₂ ^b	0.33	100	91	0	1	43	40	3	0
					10	100	0	100	0
<i>hν</i> /DCA/CH ₂ Cl ₂ /O ₂ ^b	2	100	85	0	1	96	94	2	0
<i>hν</i> /DCA/C ₆ H ₆ /O ₂ ^b	2	11	11	0	1	89	89	0	0
<i>hν</i> /NMQ ⁺ BF ₄ [–] –toluene/CH ₂ Cl ₂ /O ₂ ^c	–	7	7	0	–	28	23	0	0
Ar ₃ N ⁺ SbCl ₆ [–] (1 equiv.)/CH ₃ CN/N ₂	1	100	–	60	1	100	0	–	44
CBN (1 equiv.)/CH ₃ CN/N ₂	2	36	–	28	2	34	2	–	32
Ar ₃ N ⁺ SbCl ₆ [–] (1 equiv.)/CH ₃ CN/O ₂	1	100	0	55	1	100	0	0	57
CBN (1 equiv.)/CH ₃ CN/O ₂	2	33	9	24	2	34	5	5	24

^a Yields were determined by 200 MHz ¹H NMR analyses.

^b A 5 mL solution was irradiated with a 2 kW Xe lamp through a cut-off filter ($\lambda > 360$ nm for **5**, > 410 nm for **6**) at 20°C. [**5** or **6**]=10 mM.

^c A 2 mL solution was irradiated with a XeCl excimer laser ($\lambda = 308$ nm, 110 mJ, 10 Hz, 500 shots). [**5** or **6**]=10 mM. [NMQ⁺BF₄[–]]=1 mM, [toluene]=2 M.

**Scheme 3.**

similar pulsed irradiation under NMQ⁺BF₄[–]–toluene-cosensitized conditions under oxygen, **5** and **6** give **8** and **5**, respectively, as shown in Table 1. Similar absorption spectra with two λ_{\max} are observed for γ -ray irradiated *n*-BuCl matrices of **5** and **6** at ca. 100 and 77 K, respectively, as shown in Fig. 3. Combining the spectroscopic results with the exploratory experimental facts, the observed transient species with two λ_{\max} is assigned to **7**⁺, while a broad band (400–600 nm) observed in *n*-BuCl matrices of **5** at 77 K (Fig. 3, left, a bold line) is probably due to **5**⁺.^{‡‡}

^{‡‡} The structurally related 1,3-bis(4-methoxyphenyl)trimethylenecation radical and *cis*-1,2-bis(4-methoxyphenyl)cyclopropane cation radical were reported to exhibit λ_{\max} at 580 and 490 nm, respectively, in *n*-BuCl at 77 K.⁸

The PM3/UHF calculations indicate that indeed **5**⁺ has a local energy minimum, but **7**⁺ lies 0.9 kcal/mol lower in energy than **5**⁺.^{§§} As shown in Fig. 4,^{¶¶} **5**⁺ still

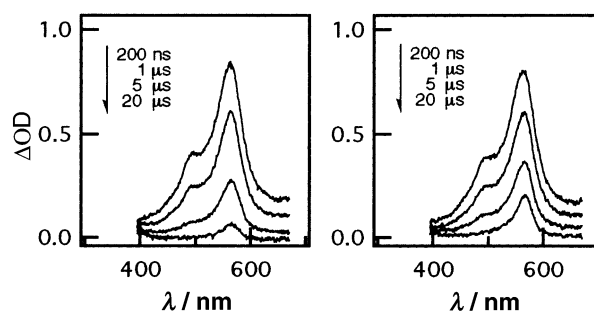


Figure 2. Nanosecond absorption spectra upon LFP of aerated CH₂Cl₂ solutions of **5** (10 mM, left) and **6** (10 mM, right) under the NMQ⁺BF₄[–] (1 mM)–toluene (2 M)–cosensitized conditions.

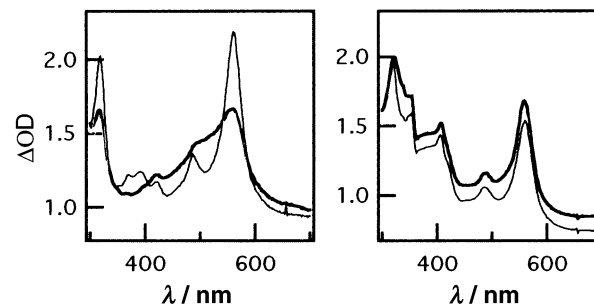


Figure 3. Absorption spectra of γ -ray irradiated *n*-BuCl matrices of **5** (10 mM, left) and **6** (10 mM, right) at 77 (bold lines) and ca. 100 K (solid lines).

^{§§} The heat of formation, ΔH_f , of **5**⁺ and **7**⁺ were calculated to be 155.26 and 154.32 kcal/mol, respectively, by using the PM3/UHF with MacGAMMESS program⁹ at C_s symmetry.

^{¶¶} Structures of **5**⁺ and **7**⁺ shown in Fig. 4 were depicted with the MacMolPlt program.¹¹

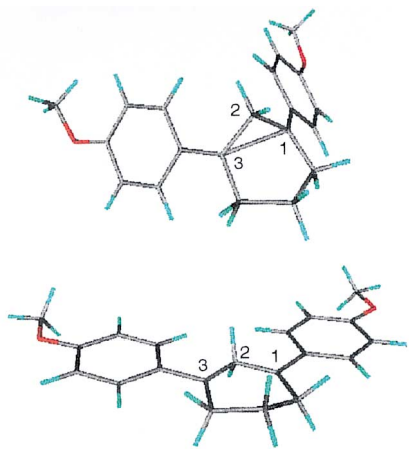


Figure 4. Structures of $5^{\bullet+}$ (top) and $7^{\bullet+}$ (bottom) optimized by PM3/UHF.

maintains the *cis*-1,2-bis(4-methoxyphenyl)cyclopropane structure with the C_1-C_3 bond length of 2.26 Å, which is longer than that (1.875 Å) of the parent cyclopropane cation radical,¹⁰ but close to the C_1-C_3 atom distance (2.52 Å) of $7^{\bullet+}$ possessing a nearly planar 1,3-bis(4-methoxyphenyl)trimethylene structure. The C_1-C_3 bond length is, therefore, long enough for $5^{\bullet+}$ to undergo cleavage to $7^{\bullet+}$ readily even at low temperature.

In conclusion, it is evident that the electron-transfer conditions employed significantly alter the reactivity of 1,3-diarylcyclohexane-1,3-diyl cation radical, demonstrating the importance of a biradical-forming BET in photoinduced electron-transfer reactions.

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