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Electron-Transfer Induced Intramolecular [2 + 2] Cycloaddition of 2,6-Diarylhepta-1,6-dienes

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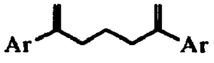
Abstract: Intramolecular [2 + 2] cycloaddition of 2,6-diaryl-1,6-heptadienes **1a—c** to bicycloheptanes **2** can be induced by electron-transfer photosensitization with 9,10-dicyanoanthracene. A stepwise mechanism involving cyclic 1,4-cation radical **3** has been proposed based on the trapping experiments.

Cyclodimerization of electron-rich alkenes can be induced by electron transfer (ET).[1] In the ET induced reactions of 1,1-diphenylethylenes, for example, 1,4-cation radicals have often been proposeed as trappable intermediates.[1, 2] Our own interest has been centered on the photoinduced ET reactions of dienes having the structure of styrene—$(CH_2)_n$—styrene,[3] from which a series of cyclic 1,4-cation radicals with different ring size may be generated. As part of the series of work, we have investigated the photoreaction of heptadienes **1** sensitized by 9,10-dicyanoanthracene (DCA), and found that the cyclization takes place in an intramolecular fashion through cyclic 1,4-cation radicals **3**.

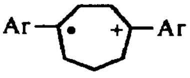
Dienes **1a—c** are good electron donors and their oxidation potentials are low enough for ET from **1** to singlet excited DCA ($^1DCA^*$) in acetonitrile. Calculations by using Weller equation[4] show that the free energy changes (ΔG) for ET from **1** to $^1DCA^*$ are exothermic by -0.83, -0.40, and -0.27 eV for **1a**, **1b**, and **1c**, respectively. In accord with this, DCA fluorescence can be efficiently quenched by **1a—c** with rate constants of near diffusion controlled. As summarized in Table 1, steady-state photolyses of 10 ml acetonitrile solutions of **1** and DCA resulted in clean reactions to afford bicycloheptanes **2a—c** with excellent material balance. The structure of **2** was determined by the spectral data.[5] For confirmation, **2c** was independently synthesized according to a literature method.[6] Bicycloheptanes **2** were stable under the photolysis conditions and apparently the transformation from **1** to **2** occurs irreversibly. In fact no formation of **1** could be observed when **2** were photolyzed in argon-saturated acetonitrile with DCA.

In order to assess the efficiency of the reaction, quantum yields of the photocycloaddition of **1** were measured. As shown in Fig. 1, linear relation was observed between the reciprocal quantum yield and the reciprocal concentration of **1**. Linear least square analysis of the plots gave the intercepts of 7.46, 1.73, and 1.89, and the



1

2



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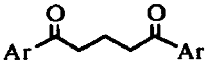

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a: Ar = 4-MeO-C_6H_4, **b**: Ar = 4-Me-C_6H_4, **c**: Ar = C_6H_5

slope values of 3.61×10^{-2}, 9.27×10^{-3} and 1.38×10^{-2} M for **1a**, **1b**, and **1c**, respectively. The intercept/slope ratios (I/S) were 207, 186, and 137 M^{-1} for **1a**, **1b**, and **1c**, respectively, which are in good agreement with the $k_q\tau$ values obtained from the DCA fluorescence quenching experiments (Table 1). From the intercepts, the limiting quantum yields of 0.13, 0.58, and 0.53 were obtained for **1a**, **1b**, and **1c**, respectively. It is remarkable that dienes **1** can undergo cyclization upon photoinduced ET with such high efficiency.[7]

Insight into the reaction mechanism was provided by similar DCA-sensitized photoreactions of **1** in oxy-

Table 1. Data of DCA Fluorescence Quenching[a] and Results of the DCA Sensitized Photoreaction of **1** in Acetonitrile.[b]

Substrate	E_{ox}[c] V *vs.* SCE	ΔG[d] eV	k_q $M^{-1}s^{-1}$	$k_q\tau$ M^{-1}	time min.	Yield / % **2**	recov.	Φ_{lim}[e]	I/S[f] M^{-1}
1a	+1.19	-0.83	1.7×10^{10}	260	30	53	45	0.13	207
1b	+1.62	-0.40	1.4×10^{10}	215	30	80	16	0.58	186
1c	+1.75	-0.27	1.1×10^{10}	162	30	76	14	0.53	137

[a] Determined by steady-state fluorescence quenching in acetonitrile. [b] A 10 ml argon-saturated solution containing 1.0×10^{-2} M of **1** and 5×10^{-4} M of DCA was photolyzed by using a 2 kW xenon lamp (λ>360 nm). [c] Oxidation potentials of **1** measured by cyclic voltammetry in acetonitrile. [d] Free energy change for ET from **1** to $^1DCA^*$. [e] Limiting quantum yield. [f] Intercept/ Slope ratio obtained from Fig. 1.

Table 2. Sensitized Photooxygenation Reaction of Dienes **1** and Bicyloheptanes **2** in Acetonitrile.

Sub-strate	Sensi-tizer	Irrad. time min.	yield / % **4**	**5**	**2**	**1**
1a	DCA	5	98	0	0	0
1a	TeCA	10	95	0	0	trace
1b	DCA	10	37	0	21	21
1b	TeCA	10	18	0	7	75
1c	DCA	30	0	0	72	0
1c[a]	DCA	30	11	5	53	0
2a	DCA	5	96	0	0	0
2a	TeCA	5	97	0	0	0
2b	DCA	60	0	0	100	0
2b	DCA	180	4	0	92	0
2c	DCA	180	0	0	98	0
2c[a]	DCA	300	10	0	79	0

A 10 ml oxygen-saturated solution of a substrate (1.0×10^{-2} M) and a sensitizer (5×10^{-4} M) was photolyzed with a 2 kW xenon lamp (λ>360 nm). [a] Photolysis with 0.1 M of $Mg(ClO_4)_2$.

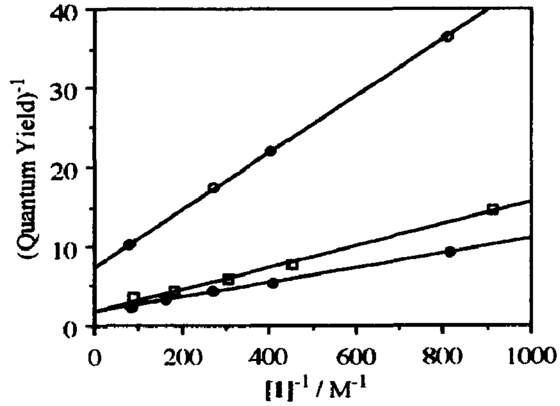


Fig. 1. Stern-Volmer plot for the DCA-sensitized photoreaction of **1a** (○), **1b** (•), and **1c** (□) in acetonitrile. Irradiations were carried out by using a 500 W xenon-Hg lamp equipped with an aqueous $CuSO_4$ filter and an interference filter (366 nm). Photolysates were analyzed by HPLC.

gen-saturated acetonitrile. As summarized in Table 2, photooxygenation of **1a** led to the formation of bicyclic peroxide **4a** as a sole product in 98% yield. This observation strongly suggests that the cyclization proceeds in a stepwise manner and 1,4-cycloheptylene cation **3a** can be produced as an intermediate by the initial cyclization of **1a**$^{\bullet+}$ at the terminals. We found that 2,6,9,10-tetracyanoanthracene (TeCA) was also effective for the photooxygenation. Since TeCA does not produce super oxide anion $O_2^{\bullet-}$, its involvement in the reaction is not necessary. Thus a mechanism involving addition of ground state O_2 to **3a** followed by back ET from a sensitizer anion radical is feasible. Similar photooxygenation of **1b** also led to the formation of peroxide **4b** together with bicycloheptane **2b**. In the case of **1c**, the formation of **2c** was prevalent. However, peroxide **4c** was obtained in 11% yield together with **2c** (53%) and diketone **5c** (5%) when 0.1 M of $Mg(ClO_4)_2$ was used.[8]

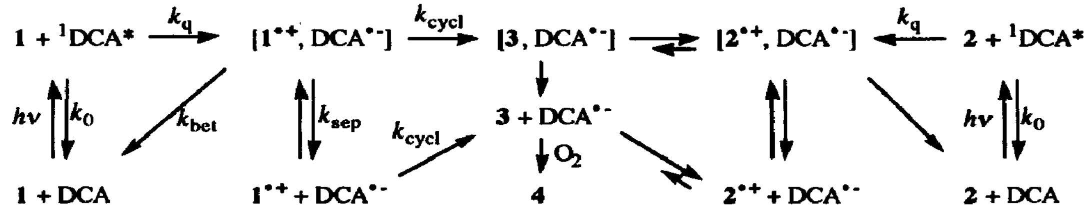
It should be noted that no or only a small amount of diketone **5** was formed in these reactions though electron-rich alkenes tend to be oxidatively cleaved under similar DCA-sensitized conditions.[9] This seems to indicate that the steady-state concentration of free cation radical **1**$^{\bullet+}$ is too low owing to the expected fast cyclization. As shown in Scheme 1, **1**$^{\bullet+}$ in photogenerated ion pairs [**1**$^{\bullet+}$, DCA$^{\bullet-}$] would undergo cyclization (k_{cycl}) in competition with the back ET deactivation (k_{bet}) and dissociation into free ion radicals (k_{sep}). Limiting quantum yields (Φ_{lim}) experimentally obtained above are expressed by eq. 1. Modification of eq. 1 leads to eq. 2, by which evaluation of k_{cycl} is possible if k_{sep} and k_{bet} are known.

$$\Phi_{lim} = \frac{k_{cycl} + k_{sep}}{k_{bet} + k_{cycl} + k_{sep}} \quad \text{--- (1)} \qquad\qquad k_{cycl} + k_{sep} = \frac{\Phi_{lim}}{1 - \Phi_{lim}}\, k_{bet} \quad \text{--- (2)}$$

While k_{sep} of 5×10^8 s^{-1} may be assumed as a constant value,[2a,10] the values of k_{bet} for the **1**—DCA systems are not available at present. However, an estimate can be made based on the reported data for photoinduced ET reactions of arene—polycyanoanthracene systems.[10] For example, the free energy change of back ET (ΔG_{bet}) for the pentamethylbenzene$^{\bullet+}$—TeCA$^{\bullet-}$ pair is -2.15 eV and its k_{bet} is determined to be 1.38×10^{10} s^{-1}. Since ΔG_{bet} for the **1a**$^{\bullet+}$— DCA$^{\bullet-}$ pair is -2.14 eV and is almost the same, the corresponding k_{bet} value should be *ca.* 1.38×10^{10} s^{-1}. Thus, k_{cycl} can be estimated to be *ca.* 1.6×10^9 s^{-1} according to eq. 2. Similarly, k_{cycl} for **1b**$^{\bullet+}$ and **1c**$^{\bullet+}$ can be estimated to be *ca.* 4.5×10^9 and 1.3×10^9 s^{-1}, respectively, based on the k_{bet} values of the *o*-xylene$^{\bullet+}$—TeCA$^{\bullet-}$ pair and the durene$^{\bullet+}$—DCA$^{\bullet-}$ pair (3.60×10^9 and 1.59×10^9 s^{-1}, respectively). The estimate suggests that cyclization of the cation radicals **1**$^{\bullet+}$ is indeed very fast and may mostly completed in the photogenerated ion pairs.

Further indication for the mechanistic scheme was obtained by the photooxygenation of **2**. As mentioned above, no reversion of **2** to **1** was observed upon photolysis with DCA in argon-saturated acetonitrile. However, when **2a** was irradiated in oxygen-saturated acetonitrile with DCA, bicyclic peroxide **4a** was obtained in near quantitative yields (Table 2). Although the yields were low, **4b** and **4c** were obtained from **2b** and **2c** by prolonged irradiation or photolysis in the presence of $Mg(ClO_4)_2$.

Scheme 1



These results suggest that **3a** can exist in equilibrium with **2a**$^{\bullet+}$ but the reversion of **3a** to **1a**$^{\bullet+}$ does not occur (Scheme 1). The reversible formation of **3b** and **3c** from **2b**$^{\bullet+}$ and **2c**$^{\bullet+}$, respectively, is also possible but in only a limited degree. Evidently, electron-donating substituents on the benzene rings seem to have some stabilizing effect on the ring-opened form **3**. Thus **3a** may stay in equilibrium with **2a**$^{\bullet+}$ as a free cation radical with relatively longer lifetime while the lifetimes of **3b** and **3c** are shorter owing to the limited formation from **2b**$^{\bullet+}$ and **2c**$^{\bullet+}$, respectively, and the efficient secondary cyclization processes, **3b, c** → **2b, c**$^{\bullet+}$.

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5 Satisfactory elemental analyses were obtained for the photoproducts and their selected spectral data are presented below. **2a**, colorless powder, mp 73 °C. MS (13.5 eV): 308 (M^+, 100%). ^{1}H-NMR (200 MHz, $CDCl_3$, δ_{ppm}): 1.90-2.03 (8H, m), 2.43 (2H, m), 3.70 (6H, s), 6.64 (4H, AA'BB'), 6.82 (4H, AA'BB'). ^{13}C-NMR (50MHz, $CDCl_3$, δ_{ppm}): 156.9 (2C), 139.3 (2C), 128.0 (4C), 112.8 (4C), 55.9 (2C), 55.1 (2C), 42.6 (2C), 29.7 (2C), 24.8 (1C). **2b**, colorless plates, mp 99 °C. MS (13.5 eV): 276 (M^+, 100%), 248 (M^+ - C_2H_4, 10%). ^{1}H-NMR (200MHz, $CDCl_3$, δ_{ppm}): 1.90-2.10 (8H, m), 2.22 (6H, s), 2.44 (2H, m), 6.80 (4H, AA'BB'), 6.89 (4H, AA'BB'). ^{13}C-NMR (50MHz, $CDCl_3$, δ_{ppm}): 144.2 (2C), 134.1 (2C), 128.1 (4C), 127.0 (4C), 56.3 (2C), 42.8 (2C), 29.9 (2C), 24.8 (1C), 20.9 (2C). **2c**, colorless powder, mp 71-72 °C (lit.[6] 72.5-73 °C). MS (13.5 eV): 248 (M^+, 100%), 220 (M^+ - C_2H_4, 16%). ^{1}H-NMR (200MHz, $CDCl_3$, δ_{ppm}) 1.92-2.38 (8H, m), 2.50 (2H, m), 6.85-7.18 (4H, m). ^{13}C-NMR (50MHz, $CDCl_3$, δ_{ppm}) 147.1 (2C), 127.4 (4C), 127.1 (4C), 124.9 (2C), 56.8 (2C), 42.5 (2C), 29.8 (2C), 24.9 (1C). **4a**, colorless needles, mp 176 °C. MS (70 eV): 340 (M^+, 6%), 312 (7%), 308 (1%), 135 (100%). ^{1}H-NMR (600MHz, CDCl3, δ_{ppm}) 1.90 (1H, dtt, J = 15.0, 6.0, 3.0 Hz), 2.03 (1H, dtt, J = 15.0, 12.0, 6.0 Hz), 2.17 (2H, ddd, J = 15.0, 6.0, 3.0 Hz), 2.29-2.39 (6H, m), 3.78 (6H, s), 6.87 (4H, AA'BB'), 7.36 (4H, AA'BB'). ^{13}C-NMR (50MHz, $CDCl_3$, δ_{ppm}) 158.6 (2C), 138.6 (2C), 125.8 (4C), 113.6 (4C), 82.5 (2C), 55.3 (2C), 40.4 (2C), 29.4 (2C), 21.3 (1C). **4b**, colorless needles, mp 186 °C. MS (70 eV): 308 (M^+, 2%), 280 (9%), 276 (1%), 119 (100%). ^{1}H-NMR (200MHz, CDCl3, δ_{ppm}): 1.80-2.52 (16H, m), 7.15 (4H, AA'BB'), 7.32 (4H, AA'BB'). ^{13}C-NMR (50MHz,$CDCl_3$, δ_{ppm}): 143.6 (2C), 136.7 (2C), 128.9 (4C), 124.4 (4C), 82.6 (2C), 40.6 (2C), 29.5 (2C), 21.3 (1C), 21.0 (2C). **4c**, colorless needles, mp 171.5-173 °C. MS (70 eV): 282 (M^+, 0.1%), 250 (0.4%), 147 (100%). ^{1}H-NMR (200 MHz, $CDCl_3$, δ_{ppm}): 1.81-2.51 (10H, m), 7.19-7.49 (10H, m). ^{13}C-NMR (50MHz, $CDCl_3$, δ_{ppm}): 146.4 (2C), 128.3 (4C), 127.1 (2C), 124.4 (4C), 82.8 (2C), 40.5 (2C), 29.4 (2C), 21.3 (1C).

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