Stepwise but Potentially Stereoselective Intramolecular [2 + 2] Cycloaddition of 2,6-Diarylocta-1,6-dienes *via* a 1,4-Cation Radical Intermediate

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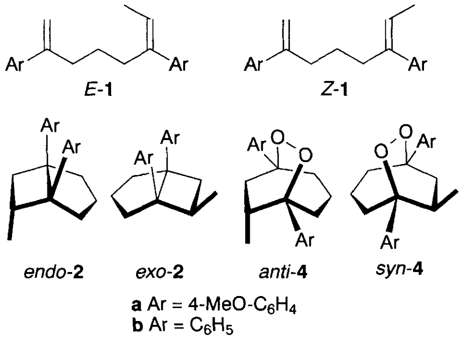
2,6-Diarylocta-1,6-dienes *E*- and *Z*-**1** undergo electron-transfer induced intramolecular [2 + 2] cycloaddition reactions to give bicycloheptanes *endo*- and *exo*-**2** through a stepwise but potentially stereoselective process.

The [2 + 2] cyclodimerization of electron-rich alkenes can be induced by electron transfer (ET).[1] In many cases, a stepwise mechanism has been proposed in which a 1,4-cation radical is involved as a trappable intermediate.[2] Although it is unlikely that such reactions are stereoselective, little work has been done on the stereochemical course of this type of reaction. It appears that the mechanism may vary with the alkenes used. Bauld *et al.*[3] and Lewis and Kojima[4] have provided examples of [2 + 2] cyclodimerizations which proceed stereoselectively in a quasi-concerted fashion.

Our own interest has been centred on the ET-induced cyclization reactions of dienes having structures of styryl–$(CH_2)_n$–styryl.[5] Recently we have investigated the stereochemistry of the photoreactions of octadienes *E*-**1** and *Z*-**1** sensitized by 9,10-dicyanoanthracene (DCA) and found that potentially stereoselective [2 + 2] cycloaddition takes place in an intramolecular fashion through cyclic 1,4-cation radicals **3**.

The dienes **1** are good electron donors and their oxidation potentials are low enough for ET from **1** to singlet excited DCA (^{1}DCA*) in acetonitrile. Calculations by using Weller's equation[6] show that the free energy changes (ΔG) for ET from **1** to ^{1}DCA* are exothermic by −0.78, −0.44, −0.59 and −0.24 eV for *E*-**1a**, *E*-**1b**, *Z*-**1a**, and *Z*-**1b**, respectively.† In accord with this, DCA fluorescence can be efficiently quenched by **1** with rate constants of 2.1×10^{10}, 1.5×10^{10}, 1.8×10^{10} and 1.2×10^{10} dm^3 mol^{-1} s^{-1}, for *E*-**1a**, *E*-**1b**, *Z*-**1a** and *Z*-**1b**, respectively.



When acetonitrile solutions of *E*-**1a** and *E*-**1b** were irradiated with DCA as a sensitizer, stereoselective intramolecular [2 + 2] cycloaddition occurred to afford the bicycloheptanes *endo*-**2a** and *endo*-**2b** with excellent material balance (Table 1, runs 1, 2).‡ Similar photoreactions with *Z*-**1a** and *Z*-**1b** also resulted in cycloaddition but afforded isomeric mixtures of bicycloheptanes *exo*-**2** and *endo*-**2** (runs 3, 4, 9). No geometric isomerization of the starting dienes, *Z*-**1** and *E*-**1**, could be observed in these reactions.

While the reactions of *Z*-**1** appeared not to be stereoselective, additional experiments under certain conditions suggested that the reactions were potentially stereoselective. First, the product *exo* : *endo* ratio in the case of the reaction of *Z*-**1a** was dependent on the irradiation time and higher ratios were obtained at shorter periods of irradiation. For example, 2.5 min irradiation resulted in the *exo* : *endo* ratio of 7 : 1, while 5 min irradiation afforded the ratio of 5.0 : 1, and 15 min gave 3.6 : 1 (Table 1, runs 5–7). These observations are due to the fact that isomerization of *exo*-**2a** to *endo*-**2a** occurs irreversibly as a secondary reaction. Control experiments showed that 60 min photolysis of *exo*-**2a** under comparable conditions afforded *endo*-**2a** in 16% yield whereas no reversion from *endo*-**2a** to *exo*-**2a** was observed.§

Secondly, when the photoreaction of *Z*-**1a** was carried out at −35 °C, the ratio increased to as high as 23 : 1 (run 8). At −35 °C, DCA-sensitized isomerization of *exo*-**2a** to *endo*-**2a** could be suppressed. In fact only 1% of *exo*-**2a** epimerized to *endo*-**2a** at this temperature. In the case of the phenyl derivative *Z*-**1b**, the product ratio *exo*-**2b** : *endo*-**2b** was not dependent on the irradiation time at room temperature and was constant at 1.1 : 1. No isomerization from *exo*-**2b** to *endo*-**2b** or interconversion between them was observed.§ However, the ratio *exo*-**2b** : *endo*-**2b** increased to 7.7 : 1 when the photoreaction of *Z*-**1b** was carried out at −35 °C (run 10).

These results indicate that the intramolecular photocycloaddition reaction of **1** proceeds stepwise through 1,4-cycloheptylene cations *a*-**3** and *e*-**3** as intermediates (Scheme 1). Upon the initial cyclization of the cation radicals $\mathbf{1}^{\cdot +}$ generated by photoinduced ET, two double bonds would be in a near parallel configuration with the two aryl groups in *syn*-like orientation. Thus *E*-$\mathbf{1}^{\cdot +}$ cyclizes to give the 1.4-cation radical *a*-**3**, whose bicyclization to *endo*-$\mathbf{2}^{\cdot +}$ followed by back-ET from DCA$^{\cdot -}$ leads to *endo*-**2**. Similarly, *Z*-$\mathbf{1}^{\cdot +}$ cyclizes to *e*-**3** and its

Table 1 Intramolecular [2 + 2] cycloaddition of **1** by photosensitization with DCA in acetonitrile[a]

Run	Substrate	*T*/°C	*t*/min	Yield (%) *exo*-**2**	Yield (%) *endo*-**2**	Yield (%) Recovery	Ratio of *exo*-**2** : *endo*-**2**
1	*E*-**1a**	rt[b]	30	0	65	35	0
2	*E*-**1b**	rt	30	0	70	24	0
3	*Z*-**1a**	rt	30	45	27	28	1.7
4	*Z*-**1a**	rt	60	47	39	14	1.2
5	*Z*-**1a**	rt	2.5	5	0.7	94	7
6	*Z*-**1a**	rt	5	10	2	88	5.0
7	*Z*-**1a**	rt	15	40	11	49	3.6
8	*Z*-**1a**	−35	60	45	2	44	23
9	*Z*-**1b**	rt	30	34	32	32	1.1
10	*Z*-**1b**	−35	300	23	3	74	7.7

[a] 10 cm^3 solutions of **1** (1.0×10^{-2} mol dm^{-3}) and DCA (4×10^{-4} mol dm^{-3}) were irradiated by using a 2 kW xenon lamp with a water IR filter and a glass filter ($\lambda > 360$ nm). [b] rt = Room temperature, *ca.* 15 °C.

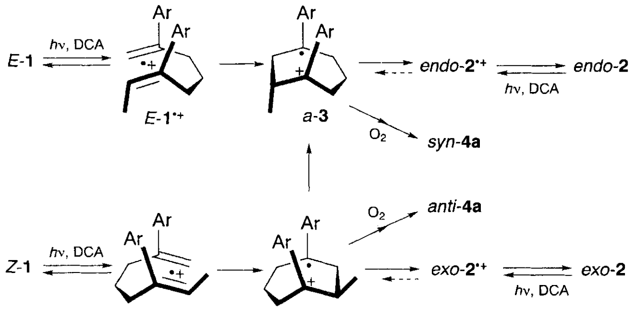
bicyclization followed by back-ET leads to *exo*-**2**. Intermediates *e*-**3** competitively undergo ring inversion to give the more stable *a*-**3** at room temperature and lead to *endo*-**2** through *endo*-**2**$^{\cdot+}$. Stereoselectivity can be much higher at lower temperatures since ring inversion is suppressed.

Further mechanistic insight was provided by similar DCA-sensitized photoreactions of *Z*- and *E*-**1** in oxygen-saturated acetonitrile. Thus 10 min irradiation of *E*-**1a** resulted in peroxide *syn*-**4a** exclusively in 65% yield. On the other hand, *Z*-**1a** gave *anti*-**4a** as a major product (33%) and *syn*-**4a** as a minor product (9%) together with *exo*-**2a** (6%) and recovered *Z*-**1a** (6%). When the photooxygenation of *Z*-**1a** was carried out at −35 °C, *anti*-**4a** (48%) was obtained in preference to *syn*-**4a** (1%).[‡]

Comparable results were observed in the photooxygenation of bicycloheptanes **2a**. Thus *syn*-**4a** was selectively obtained from *endo*-**2a** in 64% yield, indicating that *endo*-**2a**$^{\cdot+}$ is in equilibrium with *a*-**3**. While a mixture of *anti*-**4a** (44%) and *syn*-**4a** (12%) was obtained from *exo*-**2a** at room temperature, the photooxygenation at −35 °C predominantly led to *anti*-**4a** in 48% yield. Less than 1% of *syn*-**4a** could be detected by 200 MHz ^{1}H NMR.

The observed photooxygenation can be explained by a mechanism involving the trapping of 1,4-cation radicals **3a** by molecular oxygen followed by back-ET from DCA$^{\cdot-}$.[¶] Analogous mechanisms have been proposed for the formation of 1,2-dioxanes from 1,1-diphenylethylene and derivatives by several workers.[1,2] It is noteworthy that the present photooxygenation is stereoselective at low temperatures and proceeds with inversion of the stereochemistry of the 1,4-cation radicals **3a**. It is conceivable that 1,4-cation radicals **3** have a twisted boatlike ring conformation. Steric hindrance due to the two aryl groups would permit molecular oxygen to attack only from the outside.

Similar photooxygenations with phenyl derivatives **1b** and **2b** failed to give peroxides **4b**. The methoxy substituents on the benzene rings seem to have some stabilizing effects on the ring-opened intermediates **3**. Indeed, the above experiments indicate that *e*- and *a*-**3a** can exist in equilibrium with *exo*- and *endo*-**2a**$^{\cdot+}$, respectively, whereas *e*- and *a*-**3b** undergo irreversible ring closure to **2b**$^{\cdot+}$. Accordingly, intermediates **3b** should be more short-lived than **3a** and the steady-state concentration of **3b** may be too low for it to be trapped.



In summary, it is clear that *E*- and *Z*-**1** undergo ET-induced intramolecular [2 + 2] cycloaddition reactions through a stepwise but potentially stereoselective process, in which 1,4-cation radicals **3** play an important role.

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Footnotes

[†] Oxidation potentials of *E*-**1a**, *E*-**1b**, *Z*-**1a** and *Z*-**1b** are 1.22, 1.56, 1.41 and 1.76 V *vs.* SCE, respectively. Reduction potential and excitation energy of DCA are −0.95 V *vs.* SCE and 2.89 eV, respectively.

[‡] Satisfactory elementary analyses were obtained for all new compounds. The structures of *endo*-**2**, *exo*-**2**, *anti*-**4a** and *syn*-**4a** were determined on the basis of their spectral data, particularly ^{1}H NOE. Catalytic hydrogenation of *anti*-**4a** afforded the corresponding diol, whose structure was also confirmed by ^{1}H NMR with a shift reagent, Eu(fod)$_3$.

[§] In the photoreactions of **2**, no cycloreversion to dienes **1** was observed.

[¶] 2,6,9,10-Tetracyanoanthracene (TeCA) was also effective for the formation of **4a**. Since TeCA does not produce the superoxide anion $O_2^{\cdot-}$, its involvement in the reaction is not necessary.

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