PERKIN 2 COMMUNICATION

The kinetically-controlled Cope rearrangement of 2,5-bis(4-methoxyphenyl)hexa-1,5-dienes induced by photosensitised electron transfer

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The photoinduced electron-transfer Cope rearrangement of (*E*,*E*)-3,6-bis(4-methoxyphenyl)octa-2,6-diene (*E*,*E*)-1 is kinetically controlled and affords quantitatively the thermodynamically less stable (±)-3,4-dimethyl-2,5-bis(4-methoxyphenyl)hexa-1,5-diene (±)-1 at −80 °C in sharp contrast to the thermodynamically-controlled thermal Cope rearrangement.

In general, the thermal Cope rearrangement of substituted acyclic hexa-1,5-dienes is thermodynamically controlled. In fact, the thermodynamically more stable (*E*,*E*)-3,6-bis(4-methoxyphenyl)octa-2,6-diene (*E*,*E*)-**1** was quantitatively formed upon heating (±)-3,4-dimethyl-2,5-bis(4-methoxyphenyl)hexa-1,5-diene (±)-**1** at 110 °C in toluene. A sharp contrast to this thermal Cope rearrangement was found in the photoinduced electron-transfer (PET) reactions of (±)-**1** and (*E*,*E*)-**1**. The 9,10-dicyanoanthracene (DCA)-sensitised photoreactions ($\lambda > 360$ nm) of (±)-**1** and (*E*,*E*)-**1** gave nearly the same photostationary (PS) mixture of (±)-**1** and (*E*,*E*)-**1** at 20 °C in [$^2H_2$]dichloromethane or [$^2H_3$]acetonitrile. Of particular interest was the temperature-dependent change in the PS ratio. When the temperature was changed from 60 to −80 °C, (±)-**1** increased and its ratio reached an almost maximum value of 96% at −80 °C in [$^2H_2$]dichloromethane, while (*E*,*E*)-**1** decreased continuously as shown in Fig. 1.

The PET Cope rearrangement of (±)-**1** and (*E*,*E*)-**1** takes place in a radical cation cyclisation-diradical cleavage (RCCY-DRCL) mechanism† shown in Scheme 1, which includes three successive processes: the RCCY of $\mathbf{1}^{\bullet+}$ to *trans*-2,3-dimethyl-1,4-bis(4-methoxyphenyl)cyclohexane-1,4-diyl radical cation $\mathbf{2}^{\bullet+}$, back electron transfer (BET) from $\mathrm{DCA}^{\bullet-}$ to $\mathbf{2}^{\bullet+}$ and the DRCL of **2** to **1**.[1] In support of this mechanism is an energetic advantage both of forward and back ET. The generation of $\mathbf{1}^{\bullet+}$ is expected from the highly exothermic free energy change (ΔG)[2] associated with single electron transfer from **1** to the excited singlet state of DCA ($E^{\mathrm{red}}_{\frac{1}{2}} = -0.95$ V *vs.* SCE in acetonitrile) as shown in Table 1. In fact, the fluorescence of DCA was quenched efficiently with the large Stern–Volmer constants ($k_q\tau$) even in dichloromethane. BET from $\mathrm{DCA}^{\bullet-}$ to $\mathbf{2}^{\bullet+}$ is also calculated to be exothermic by $\Delta G_{\mathrm{BET}} = -78.2$ kJ mol^{-1} in acetonitrile, on the assumption that $E^{\mathrm{ox}}_{\frac{1}{2}}$ of **2** is comparable with that of the 4-methoxycumyl radical ($E^{\mathrm{ox}}_{\frac{1}{2}} = -0.14$ V *vs.* SCE in acetonitrile).[3] However, prolonged irradiation of DCA with *trans*-2,3-dimethyl-1,4-bis(4-methoxyphenyl)bicyclo[2.2.0]hexane **3** in [$^2H_2$]dichloromethane at 20 °C gave the 61 : 39 PS mixture of (±)-**1** and (*E*,*E*)-**1**, which is nearly the same as the Cope PS mixture. This result indicates that $\mathbf{3}^{\bullet+}$ successively rearranged to $\mathbf{2}^{\bullet+}$, **2** and a mixture of (±)-**1** and (*E*,*E*)-**1** which, in turn, entered into the PET Cope rearrangement cycle (Scheme 1), giving rise to the same PS mixture.

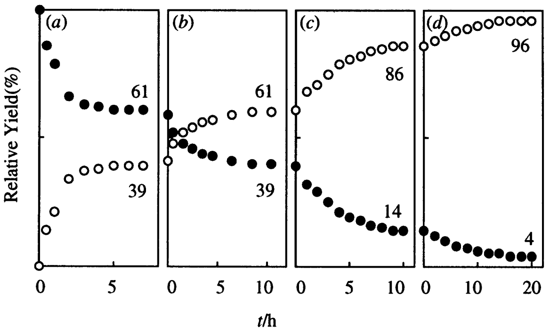
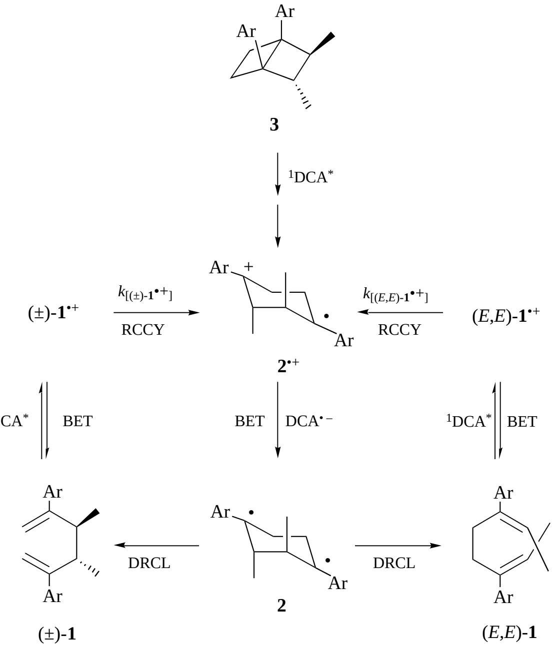


Fig. 1 Temperature-dependent changes in photostationary ratio of the PET Cope rearrangement of (±)-**1** (○) and (*E*,*E*)-**1** (●); (*a*) 60 °C, (*b*) 20 °C, (*c*) −30 °C, (*d*) −80 °C



Scheme 1 A RCCY-DRCL mechanism for the PET Cope rearrangement of (±)-**1** and (*E*,*E*)-**1** (Ar = 4-MeOC$_6$H$_4$)

However, in the PET reaction of **3** it was found that the ratio of (±)-**1** and (*E*,*E*)-**1** at low conversion (2–15%) did not depend upon temperature,‡ unlike a PS ratio of the PET Cope rearrangement. In addition, there was no difference in $k_q\tau$ between (±)-**1** and (*E*,*E*)-**1** at −80 °C (Table 1). Consequently, the initial RCCY step was assumed to be responsible for the

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† A full detail of the RCCY-DRCL mechanism of the PET degenerate Cope rearrangement of 2,5-diarylhexa-1,5-dienes will be published soon.

‡ The observed ratios of (±)-**1** and (*E*,*E*)-**1** were 29 : 71 (at 2–13% conversion), 32 : 68 (2–8%), 27 : 73 (3–14%), 32 : 68 (1–10%), 31 : 69 (2–15%), 35 : 65 (2–8%), 33 : 67 (2–9%) and 35 : 65 (6%) at 60, 50, 40, 30, 20, 0, −30 and −80 °C, respectively.

Table 1 Oxidation potentials ($E_{\frac{1}{2}}^{\mathrm{ox}}$) of **1**, free energy changes (ΔG) associated with electron transfer with ^{1}DCA* and the Stern–Volmer constants ($k_{\mathbf{q}}\tau$) for the DCA-fluorescence quenching

			$k_{\mathbf{q}}\tau^c$/M^{-1}	
	$E_{\frac{1}{2}}^{\mathrm{ox}\,a}$/V	ΔG^b/kJ mol^{-1}	20 °C	−80 °C
(±)-**1**	+1.31	−62.7	165	35
(*E*,*E*)-**1**	+1.11	−82.7	205	33

^{a} *vs*. SCE in acetonitrile, scan rate 100 mV s^{-1}. ^{b} In acetonitrile. See ref. 2. ^{c} In dichloromethane.

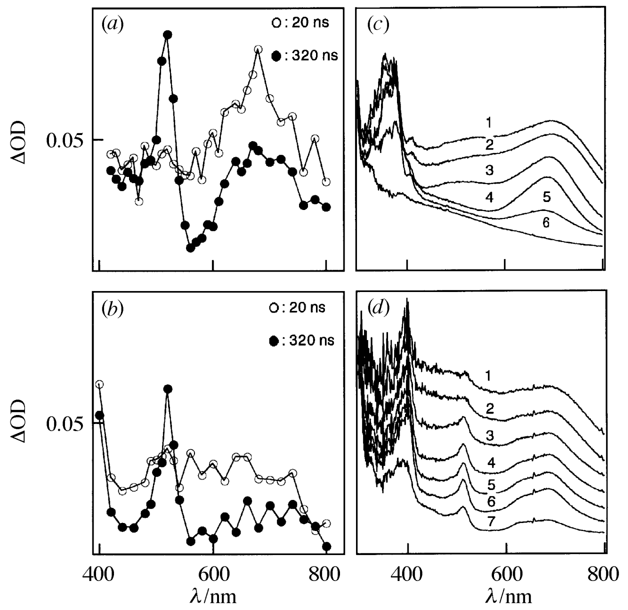

Fig. 2 (*a*) Transient absorption spectra after pulse irradiation of 1,2-dichloroethane solutions of (±)-**1** and (*b*) (*E*,*E*)-**1** at 20 °C. (*c*) Absorption spectra of γ-ray irradiated butyl chloride matrices of (±)-**1** and (*d*) (*E*,*E*)-**1** at 77 K (1) and during annealing (2–6 or 7).

observed temperature-dependency of the PS ratio in the PET Cope rearrangement and not the difference in efficiency to form (±)-$\mathbf{1}^{\cdot+}$ and (*E*,*E*)-$\mathbf{1}^{\cdot+}$, and thus the cyclisations of (±)-$\mathbf{1}^{\cdot+}$ and (*E*,*E*)-$\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$ were kinetically investigated by pulse radiolysis.§

As shown in Fig. 2(*a*) and (*b*), pulse radiolyses of (±)-**1** and (*E*,*E*)-**1** in 1,2-dichloroethane exhibited a sharp absorption with $\lambda_{\mathbf{max}}$ at 515 nm due to $\mathbf{2}^{\cdot+}$ and a broad absorption band with $\lambda_{\mathbf{max}}$ at 680–700 nm due to (±)-$\mathbf{1}^{\cdot+}$ or (*E*,*E*)-$\mathbf{1}^{\cdot+}$. The transient absorption due to $\mathbf{2}^{\cdot+}$ was also observed by laser flash photolyses of (±)-**1** or (*E*,*E*)-**1** under the DCA-sensitised conditions using biphenyl as a cosensitiser in degassed acetonitrile. These assignments were made by comparison with transient absorption maxima of 2,5-bis(4-methoxyphenyl)hexane-2,5-diyl radical cation ($\lambda_{\mathbf{max}} = 520$ nm in 1,2-dichloroethane),[4a] 1,4-bis-(4-methoxyphenyl)cyclohexane-1,4-diyl radical cation ($\lambda_{\mathbf{max}} = 520$ nm in butyl chloride),[4b] α-methyl-4-methoxystyrene radical cation ($\lambda_{\mathbf{max}} = 660$ nm in 4 : 1 water–acetonitrile)[4c] and 2,5-bis(4-methoxyphenyl)hexa-1,5-diene radical cation ($\lambda_{\mathbf{max}} = 680$ nm in butyl chloride).¶,[4b] Consequently, a sharp absorption appeared as a broad absorption diminished in pulse radiolyses, indicating that the initially formed (±)-$\mathbf{1}^{\cdot+}$ and (*E*,*E*)-$\mathbf{1}^{\cdot+}$ readily cyclise to a common intermediate $\mathbf{2}^{\cdot+}$. Rate constants, $k_{\mathbf{obs}}$, for the RCCY of (±)-$\mathbf{1}^{\cdot+}$ and (*E*,*E*)-$\mathbf{1}^{\cdot+}$ were obtained by analyses of the time-dependent change of absorption intensity at 520 nm. From the Arrhenius plot of $k_{\mathbf{obs}}$ between 10 and 50 °C, rate constants, $k_{\mathbf{est}}$, for the RCCY at 60 and −80 °C were estimated and listed in Table 2 together with activation parameters for the RCCY of (±)-$\mathbf{1}^{\cdot+}$ and (*E*,*E*)-$\mathbf{1}^{\cdot+}$.‖ Enthalpies of activation ($\Delta H^{\ddagger}$) for (±)-$\mathbf{1}^{\cdot+}$ and (*E*,*E*)-$\mathbf{1}^{\cdot+}$ are small as expected from the MINDO/3 calculation[5] of Bauld *et al.* for the parent hexa-1,5-diene radical cation, but the value for (±)-$\mathbf{1}^{\cdot+}$ is 3.1 kJ mol^{-1} larger than that of (*E*,*E*)-$\mathbf{1}^{\cdot+}$. Accordingly, both (±)-$\mathbf{1}^{\cdot+}$ and (*E*,*E*)-$\mathbf{1}^{\cdot+}$ cyclise to $\mathbf{2}^{\cdot+}$ with nearly the same rate constant at 60 °C, but (±)-$\mathbf{1}^{\cdot+}$ cyclises three times slower than (*E*,*E*)-$\mathbf{1}^{\cdot+}$ at −80 °C, indicating the retardation of the RCCL of (±)-$\mathbf{1}^{\cdot+}$ at lower temperature. In fact, γ-ray irradiation studies in low temperature matrices revealed that (±)-$\mathbf{1}^{\cdot+}$ decayed without the formation of $\mathbf{2}^{\cdot+}$ during annealing from 77 to *ca.* 100 K, whereas (*E*,*E*)-$\mathbf{1}^{\cdot+}$ decayed forming $\mathbf{2}^{\cdot+}$ upon similar annealing [Fig. 2(*c*) and (*d*)].** A plausible explanation for the temperature-dependent change in the PS ratio is thus the lower reactivity of (±)-$\mathbf{1}^{\cdot+}$ relative to (*E*,*E*)-$\mathbf{1}^{\cdot+}$, which results in the accumulation of (±)-**1** in the Cope PS mixture as the temperature is lowered. The repeating formations of $\mathbf{2}^{\cdot+}$ with small $\Delta H^{\ddagger}$ and **2** by highly exothermic BET in the PET Cope rearrangement cycle are thus important key processes for the PET Cope rearrangement to occur even at −80 °C.

Table 2 Kinetic parameters for cyclisation of $\mathbf{1}^{\cdot+}$ in 1,2-dichloroethane

	$\Delta H^{\ddagger}_{(\mathbf{20}\,°\mathrm{C})}$/ kJ mol^{-1}	$A/10^{10}$ s^{-1}	$\Delta S^{\ddagger}_{(\mathbf{20}\,°\mathrm{C})}$/ J mol^{-1} K^{-1}	$k_{\mathbf{est}}$/s^{-1}	
				60 °C	−80 °C
(±)-$\mathbf{1}^{\cdot+}$	16.9 ± 1.2	14 ± 5	−39.9	1.3 × 10^8	8.0 × 10^5
(*E*,*E*)-$\mathbf{1}^{\cdot+}$	13.8 ± 1.1	5.7 ± 3.0	−47.2	1.6 × 10^8	2.4 × 10^6

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§ A pair of 1,2-dichloroethane solutions of (±)-**1** and (*E*,*E*)-**1** (10 mM) was deaerated by argon saturation and simultaneously irradiated with electron pulses from an L-band linear accelerator of Osaka University (28 MeV, 8 ns pulse width).

¶ A plausible explanation of the absorption with $\lambda_{\mathbf{max}}$ at 515 nm will be separately reported by three of the authors (A. I., S. T. and S. T.).

‖ $E_{\mathbf{a}}$ values and *A*-factors shown in Table 2 were obtained as an average of four separate runs. The face values of $E_{\mathbf{a}}$ and *A* are as follows: $E_{\mathbf{a}(\pm)\text{-}\mathbf{1}} = 16.2$, 21.7, 20.7 and 18.8 kJ mol^{-1}, $E_{\mathbf{a}(E,E)\text{-}\mathbf{1}} = 14.3$, 17.3, 18.9 and 14.4 kJ mol^{-1}; $A_{(\pm)\text{-}\mathbf{1}} = 3.64$, 22.6, 20.6 and 8.08 × 10^{10} s^{-1}, and $A_{(E,E)\text{-}\mathbf{1}} = 1.85$, 5.11, 14.3 and 1.61 × 10^{10} s^{-1}, respectively.

** A sample solution (10 mM) was degassed by repeating three freeze–pump–thaw cycles and irradiated with γ-ray from a 370 TBq ^{60}Co source at 77 K.

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