

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 (\pm)-3,4-dimethyl-2,5-bis(4-methoxyphenyl)hexa-1,5-diene (\pm)-**1** at $-80\text{ }^\circ\text{C}$ 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 (\pm)-3,4-dimethyl-2,5-bis(4-methoxyphenyl)hexa-1,5-diene (\pm)-**1** at $110\text{ }^\circ\text{C}$ in toluene. A sharp contrast to this thermal Cope rearrangement was found in the photoinduced electron-transfer (PET) reactions of (\pm)-**1** and (*E,E*)-**1**. The 9,10-dicyanoanthracene (DCA)-sensitised photo-reactions ($\lambda > 360\text{ nm}$) of (\pm)-**1** and (*E,E*)-**1** gave nearly the same photostationary (PS) mixture of (\pm)-**1** and (*E,E*)-**1** at $20\text{ }^\circ\text{C}$ in [$^2\text{H}_2$]dichloromethane or [$^2\text{H}_3$]acetonitrile. Of particular interest was the temperature-dependent change in the PS ratio. When the temperature was changed from 60 to $-80\text{ }^\circ\text{C}$, (\pm)-**1** increased and its ratio reached an almost maximum value of 96% at $-80\text{ }^\circ\text{C}$ in [$^2\text{H}_2$]dichloromethane, while (*E,E*)-**1** decreased continuously as shown in Fig. 1.

The PET Cope rearrangement of (\pm)-**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 $1^{+\cdot}$ to *trans*-2,3-dimethyl-1,4-bis(4-methoxyphenyl)cyclohexane-1,4-diyl radical cation $2^{+\cdot}$, back electron transfer (BET) from DCA $^{\cdot-}$ to $2^{+\cdot}$ 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 $1^{+\cdot}$ 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 ($E_{\text{red}}^{\text{red}} = -0.95\text{ V vs. SCE}$ 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 DCA $^{\cdot-}$ to $2^{+\cdot}$ is also calculated to be exothermic by $\Delta G_{\text{BET}} = -78.2\text{ kJ mol}^{-1}$ in acetonitrile, on the assumption that $E_{\text{ox}}^{\text{ox}}$ of **2** is comparable with that of the 4-methoxycumyl radical ($E_{\text{ox}}^{\text{ox}} = -0.14\text{ V vs. SCE}$ 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 [$^2\text{H}_2$]dichloromethane at $20\text{ }^\circ\text{C}$ gave the 61:39 PS mixture of (\pm)-**1** and (*E,E*)-**1**, which is nearly the same as the Cope PS mixture. This result indicates that $3^{+\cdot}$ successively rearranged to $2^{+\cdot}$, **2** and a mixture of (\pm)-**1** and (*E,E*)-**1** which, in turn, entered into the PET Cope rearrangement cycle (Scheme 1), giving rise to the same PS mixture.

† 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.

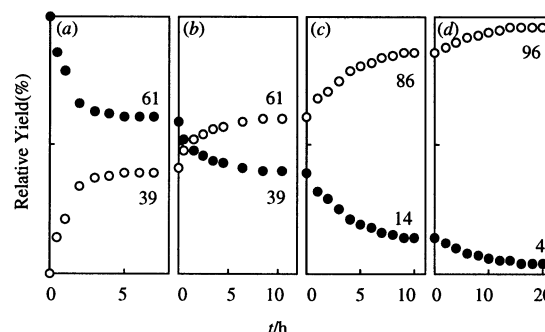
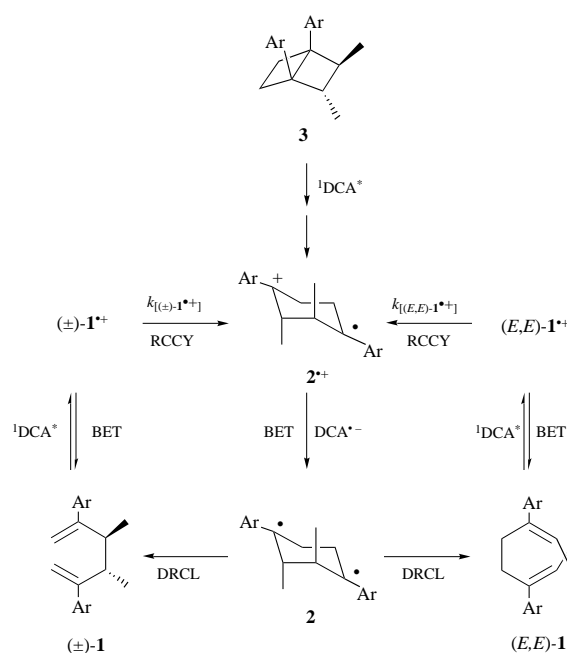


Fig. 1 Temperature-dependent changes in photostationary ratio of the PET Cope rearrangement of (\pm)-**1** (○) and (*E,E*)-**1** (●); (a) $60\text{ }^\circ\text{C}$, (b) $20\text{ }^\circ\text{C}$, (c) $-30\text{ }^\circ\text{C}$, (d) $-80\text{ }^\circ\text{C}$



Scheme 1 A RCCY-DRCL mechanism for the PET Cope rearrangement of (\pm)-**1** and (*E,E*)-**1** (Ar = 4-MeOC₆H₄)

However, in the PET reaction of **3** it was found that the ratio of (\pm)-**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 (\pm)-**1** and (*E,E*)-**1** at $-80\text{ }^\circ\text{C}$ (Table 1). Consequently, the initial RCCY step was assumed to be responsible for the

‡ The observed ratios of (\pm)-**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 $-80\text{ }^\circ\text{C}$, respectively.

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

	$E_{1/2}^{\text{ox}}/V$	$\Delta G^b/kJ\ mol^{-1}$	$k_q\tau^c/M^{-1}$	
			20 °C	-80 °C
(±)- 1	+1.31	-62.7	165	35
(<i>E,E</i>)- 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.

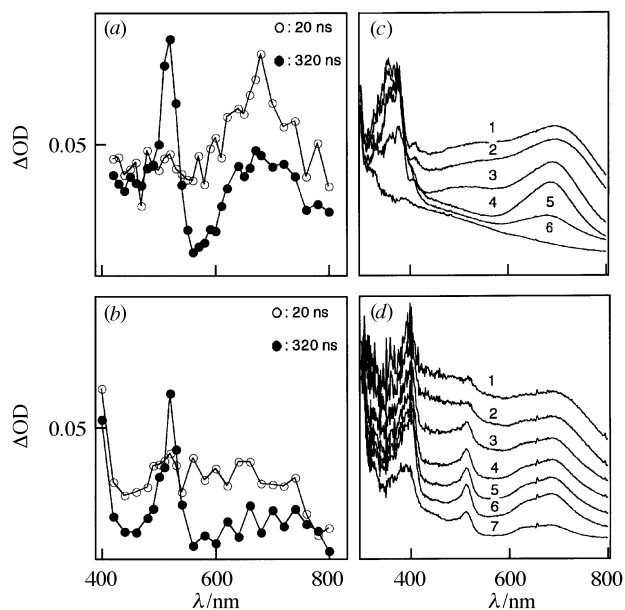


Fig. 2 (a) Transient absorption spectra after pulse irradiation of 1,2-dichloroethane solutions of (±)-**1** and (b) (*E,E*)-**1** at 20 °C. (c) Absorption spectra of γ -ray irradiated butyl chloride matrices of (±)-**1** and (*E,E*)-**1** at 77 K (1) and during annealing (2–6 or 7).

observed temperature-dependency of the PS ratio in the PET Cope rearrangement and not the difference in efficiency to form (±)-**1**^{•+} and (*E,E*)-**1**^{•+}, and thus the cyclisations of (±)-**1**^{•+} and (*E,E*)-**1**^{•+} to **2**^{•+} 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 λ_{max} at 515 nm due to **2**^{•+} and a broad absorption band with λ_{max} at 680–700 nm due to (±)-**1**^{•+} or (*E,E*)-**1**^{•+}. The transient absorption due to **2**^{•+} 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 ($\lambda_{\text{max}} = 520$ nm in 1,2-dichloroethane),^{4a} 1,4-bis(4-methoxyphenyl)cyclohexane-1,4-diyl radical cation ($\lambda_{\text{max}} = 520$ nm in butyl chloride),^{4b} α -methyl-4-methoxystyrene radical cation ($\lambda_{\text{max}} = 660$ nm in 4:1 water-acetonitrile)^{4c} and 2,5-bis(4-methoxyphenyl)hexa-1,5-diene radical cation ($\lambda_{\text{max}} = 680$ nm in butyl chloride).[¶] Consequently, a sharp absorption appeared as a broad absorption diminished in pulse radiolyses, indicating that the initially formed (±)-**1**^{•+} and (*E,E*)-**1**^{•+} readily cyclise to a common intermediate **2**^{•+}. Rate constants, k_{obs} , for the RCCY of (±)-**1**^{•+} and (*E,E*)-**1**^{•+} were obtained by analyses of the time-

[§] 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 λ_{max} at 515 nm will be separately reported by three of the authors (A. I., S. T. and S. T.).

Table 2 Kinetic parameters for cyclisation of **1**^{•+} in 1,2-dichloroethane

	$\Delta H_{20}^{\ddagger}/kJ\ mol^{-1}$	$A/10^{10}\ s^{-1}$	$\Delta S_{20}^{\ddagger}/J\ mol^{-1}\ K^{-1}$	k_{est}/s^{-1}	
				60 °C	-80 °C
(±)- 1 ^{•+}	16.9 ± 1.2	14 ± 5	-39.9	1.3 × 10 ⁸	8.0 × 10 ⁵
(<i>E,E</i>)- 1 ^{•+}	13.8 ± 1.1	5.7 ± 3.0	-47.2	1.6 × 10 ⁸	2.4 × 10 ⁶

dependent change of absorption intensity at 520 nm. From the Arrhenius plot of k_{obs} between 10 and 50 °C, rate constants, k_{est} , for the RCCY at 60 and -80 °C were estimated and listed in Table 2 together with activation parameters for the RCCY of (±)-**1**^{•+} and (*E,E*)-**1**^{•+}. Enthalpies of activation (ΔH^{\ddagger}) for (±)-**1**^{•+} and (*E,E*)-**1**^{•+} are small as expected from the MINDO/3 calculation⁵ of Bauld *et al.* for the parent hexa-1,5-diene radical cation, but the value for (±)-**1**^{•+} is 3.1 kJ mol⁻¹ larger than that of (*E,E*)-**1**^{•+}. Accordingly, both (±)-**1**^{•+} and (*E,E*)-**1**^{•+} cyclise to **2**^{•+} with nearly the same rate constant at 60 °C, but (±)-**1**^{•+} cyclises three times slower than (*E,E*)-**1**^{•+} at -80 °C, indicating the retardation of the RCCL of (±)-**1**^{•+} at lower temperature. In fact, γ -ray irradiation studies in low temperature matrices revealed that (±)-**1**^{•+} decayed without the formation of **2**^{•+} during annealing from 77 to ca. 100 K, whereas (*E,E*)-**1**^{•+} decayed forming **2**^{•+} 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 (±)-**1**^{•+} relative to (*E,E*)-**1**^{•+}, which results in the accumulation of (±)-**1** in the Cope PS mixture as the temperature is lowered. The repeating formations of **2**^{•+} with small ΔH^{\ddagger} and ΔS^{\ddagger} 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.

Acknowledgements

We gratefully acknowledge financial support from the Ministry of Education, Science, Culture and Sports (Grant-in-Aid for Scientific Research Nos. 03303001, 03403005, 05740439 and 08740560).

^{||} E_a values and A -factors shown in Table 2 were obtained as an average of four separate runs. The face values of E_a and A are as follows: $E_{a(\pm)\text{-}1} = 16.2, 21.7, 20.7$ and 18.8 kJ mol⁻¹, $E_{a(E,E)\text{-}1} = 14.3, 17.3, 18.9$ and 14.4 kJ mol⁻¹; $A_{(\pm)\text{-}1} = 3.64, 22.6, 20.6$ and 8.08×10^{10} s⁻¹, and $A_{(E,E)\text{-}1} = 1.85, 5.11, 14.3$ 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 ⁶⁰Co source at 77 K.

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Paper 7/01043E

Received 13th February 1997

Accepted 19th February 1997