

Striking Contrast between Photoinduced and Non-photoinduced Electron-transfer Reactions of 1,4-Diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene

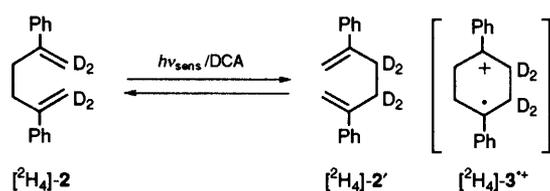
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Photoinduced electron-transfer (PET) reactions of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene **1** result in a quantitative formation of 2,5-diphenylhexa-1,5-diene **2**, in sharp contrast to the results of non-PET reactions and showing the importance of a back electron-transfer (BET) process in PET reactions.

Adam and coworkers reported¹ that the cerium(IV) ammonium nitrate, [Ce(NH₄)₂(NO₃)₆] (CAN) catalysed deazetation of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene **1** afforded 1,4-diphenylcyclohexane-1,4-diyl cation radical **3**^{•+}, but **3**^{•+} did not undergo cleavage to 2,5-diphenylhexa-1,5-diene **2**. According to calculations by Bauld *et al.* ring cleavage of cyclohexane-1,4-diyl cation radical has a high activation energy,² failure in the cleavage of **3**^{•+} appears reasonable. In contrast, the 9,10-dicyanoanthracene (DCA)-sensitised electron-transfer photoreaction of [2H₄]-**2** involved degenerate Cope rearrangement in which [2H₄]-**3**^{•+} intervenes as an intermediate (Scheme 1).^{3a-d} If the PET degenerate Cope is involved by the direct cleavage of [2H₄]-**3**^{•+} in a cyclisation-cleavage mechanism, the reactivity of **3**^{•+} under PET conditions is apparently inconsistent with that under non-PET conditions. It is thus of particular interest to explain this inconsistency in order to know whether or not the ring cleavage in the PET degenerate Cope rearrangement of [2H₄]-**2** occurs on the cation-radical energy surface.^{3e} We have examined the deazetation of diazene **1** under various electron-transfer conditions,[†] and we now report that PET reactions of **1** result in quantitative formation of **2**, in sharp contrast to non-PET reactions.

Results for various electron-transfer reactions of **1** are summarized in Table 1 together with results reported previously.⁴ Like the CAN-catalysed reaction, non-PET reactions such as the cerium(IV) tetra-*n*-butylammonium nitrate (CBN),⁵ tris(4-bromophenyl)aminium hexachloroantimonate and electrode catalysed reactions of **1** gave *p*-terphenyl **4** in moderate yields without the formation of **2**. In contrast, the



Scheme 1 The PET degenerate Cope rearrangement

PET reaction of **1** afforded **2**, but no **4** at all. Upon irradiation ($\lambda > 410$ nm) of DCA with **1** in MeCN, CH₂Cl₂, and C₆H₆ under N₂ at ambient temperature, **2** was produced quantitatively. Because **1** [$E^{\text{ox}}_{1/2} = +1.16$ V vs. SCE in MeCN[‡]] efficiently quenched the DCA fluorescence with rate constants, k_q , of 1.62, 1.22 and 1.14×10^{10} dm³ mol⁻¹ s⁻¹ in MeCN, CH₂Cl₂ and C₆H₆, respectively, and the free energy change (ΔG) for a single electron transfer (SET) from **1** to ¹DCA* was large and negative (-77 kJ mol⁻¹) in MeCN,[§] PET to form **1**^{•+} must be operative under the DCA-sensitised conditions. In fact, **1** was quantitatively recovered when irradiated with light of similar wavelength in the absence of DCA. Almost the same result was obtained in photoexcitations of the electron donor-acceptor complex of **1** and 1,2,4,5-tetracyanobenzene (TCNB) or tetracyanoethylene (TCNE)[¶] in CH₂Cl₂ as shown in Table 1.

Deazetation reactions of **1** under PET conditions (entries 5–7) thus provided the same results as those under pyrolytic,^{4a} direct irradiation^{4b} and benzophenone (BP)-sensitised^{4c} conditions (entries 8–10) where diyl **3** serves as a key intermediate, but are different from deazetations under non-PET conditions (entries 1–4). Because both PET and non-PET reactions of **1** are reasonably assumed to generate **3**^{•+} via **1**^{•+}, one probable explanation for the striking difference between PET and non-PET processes lies in the question whether or not a back electron transfer (BET) from a reduced species to **3**^{•+} efficiently operates to form diyl **3** (Scheme 2). In PET reactions, BET processes are energetically favourable. On the basis of redox potentials[‡] of cumyl radical ($E^{\text{ox}}_{1/2} = +0.16$ V vs. SCE in MeCN)⁶ and the electron acceptors ($E^{\text{red}}_{1/2} = -0.95$ V for DCA, -0.70 V for TCNB and $+0.22$ V for TCNE), free energy changes (ΔG_{BET}) for the formation of **3** and acceptors from ion radical pair [**3**^{•+}-acceptor^{•-}] are calculated to be -107 , -83 and 5.8 kJ mol⁻¹, respectively, for DCA, TCNB and TCNE. Cation radical **3**^{•+} generated under PET conditions thus suffers a rapid BET from DCA^{•-}, TCNB^{•-} and TCNE^{•-} to form **3**, through which a low-energy ring cleavage takes place to form **2**.⁷

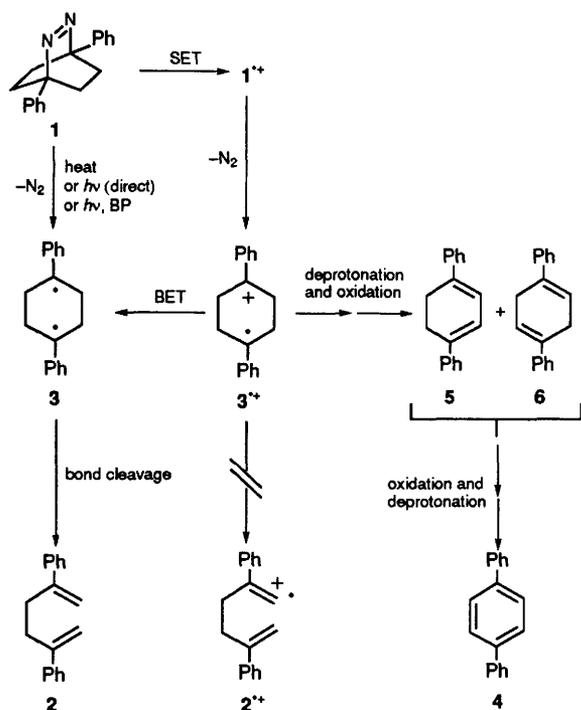
On the other hand, in non-PET reactions such as the CAN-, CBN- and aminium salt-catalysed reactions, BET processes from Ce^{III} and (4-BrC₆H₄)₃N to **3**^{•+} are highly endothermic as

Table 1 Deazetation reactions of **1** under various conditions

Entry	Conditions	Solvent	Conv. (%)	Yields ^a (%)	
				2	4
1	CAN, Bu ⁿ ₄ NHSO ₄ ^b	CHCl ₃	100	0	46
2	CBN (1 equiv.)	CH ₂ Cl ₂	55	0	18 ^c
3	(4-BrC ₆ H ₄) ₃ N ^{•+} SbCl ₆ ⁻ (2 equiv.)	CH ₂ Cl ₂	40	0	29
4	Electrolysis (+1.25 V)	CH ₂ Cl ₂	39	0	11
5	$h\nu_{\text{sens}}$ ($\lambda > 410$ nm), DCA	CH ₂ Cl ₂	100	100	0
6	$h\nu_{\text{CT}}$ ($\lambda > 410$ nm), TCNB	CH ₂ Cl ₂	100	100	0
7	$h\nu_{\text{CT}}$ ($\lambda > 410$ nm), TCNE	CH ₂ Cl ₂	92	40	0
8	Heat ^d (110 °C)	PhMe	100	100	0
9	$h\nu$ (direct, ^e $\lambda > 320$ nm)	C ₆ H ₆	100	100	0
10	$h\nu$ ($\lambda = 333$ nm), BP ^f	C ₆ H ₆	100	100 ^g	0

^a This work except for entries 1 and 10. ^b Ref. 1. ^c Including the yield for **5** (11%) and **6** (3%). ^d Ref. 4(a). ^e Ref. 4(b). ^f Ref. 4(c).

^g Including the yield for 1,4-diphenylbicyclo[2.1.1]hexane.

Scheme 2 Mechanisms for deazetation reactions of **1**

calculated free energy changes [$\Delta G_{\text{BET}} = \text{ca. } 70 \text{ kJ mol}^{-1}$ for Ce^{III} and 86 kJ mol^{-1} for $(4\text{-BrC}_6\text{H}_4)_3\text{N}$] indicate.[‡] Under non-PET conditions BET form **3** is thus unlikely, and 3^{2+} is converted to **4** by successive deprotonation-oxidation steps¹ via 1,4-diphenylcyclohexa-1,3-diene **5** and 1,4-diphenylcyclohexa-1,4-diene **6**.^{||} This was confirmed by the fact that **5** (11%) and **6** (3%) were formed concurrently in the CBN-catalysed oxidation and that independent aminium-catalysed oxidation of **5** afforded **4** in 70% yield.

In summary, results shown here demonstrate the dual reactivity of **1** under PET and non-PET conditions which results in a complementary product distribution. Similar product distributions among PET reactions, pyrolysis and direct irradiation of **1** stress the importance of BET to form **3** from 3^{2+} under PET conditions and further suggest the operation of the same process in the PET degenerate Cope rearrangement of $[^2\text{H}_4]\text{-2}$ which does not occur under non-PET conditions such as the CBN-, aminium salt-catalysed oxidations, pulse radiolysis and γ -ray irradiation in a low-temperature matrix.^{††}

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Footnotes

[†] Recently, Adam and coworkers reported the comparison of PET and non-PET reactions of alkyl-substituted 2,3-diazabicyclo[2.2.1]hept-2-enes.⁸

[‡] Redox potentials ($E^{\text{red}}_{1/2}$ and $E^{\text{ox}}_{1/2}$) were measured by cyclic voltammetry at a platinum electrode in dry MeCN with 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte. The $E^{\text{red}}_{1/2}$ values for CAN and CBN, and $E^{\text{ox}}_{1/2}$ for $(4\text{-BrC}_6\text{H}_4)_3\text{N}$ are ca. +0.86, ca. +0.90 and +1.05 V, respectively, in MeCN.

[§] The free energy change (ΔG) was calculated by using the Rehm-Weller equation^{9a,b}: $\Delta G/\text{kJ mol}^{-1} = 96.5 [E^{\text{ox}}_{1/2}(\text{1}) - E^{\text{red}}_{1/2}(\text{DCA}) - E_{0-0}] - e^2/\epsilon r$, where $E^{\text{ox}}_{1/2}(\text{1})$ is +1.16 V vs. SCE, $E^{\text{red}}_{1/2}(\text{DCA})$ is -0.95 V, E_{0-0} is 2.91 eV in MeCN and the coulombic term ($e^2/\epsilon r$) was ignored after Farid's example.^{9c}

[¶] A control experiment of **2** and TCNE under similar photoconditions resulted in their recovery in 40 and 36% yield, respectively. In addition, several unidentified peaks which are also seen for **1** and TCNE were observed in the ^1H NMR spectrum. Consequently, we can ascribe the low yield of **2** in entry 7 to secondary decomposition of **2** and TCNE.

^{||} Because cyclohexene cation radical is readily produced even in Freon matrices by the 1,3-hydrogen shift from cyclohexane-1,4-diyli cation radical formed upon the γ -ray irradiation of hexa-1,5-diene,^{10a} bicyclo[2.2.0]hexane,^{10b} and 2,3-diazabicyclo[2.2.2]oct-2-ene,^{10c,d} there might be a bypass through which *p*-terphenyl **4** is formed from 1,4-diphenylcyclohexene cation radical.

^{††} Unpublished results. We shall soon give full details of the diyli contribution to the PET reaction of **1** and the PET degenerate Cope rearrangement of $[^2\text{H}_4]\text{-2}$.

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