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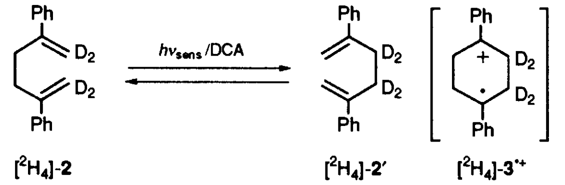
Photoinduced electron-transfer (PET) reactions of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene **1** result in a quantitative formation of 2,5-diphenylhexa-1,5-diene **2**, in sharp contrast to the results of non-PET reactions and showing the importance of a back electron-transfer (BET) process in PET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

Adam and coworkers reported[1] that the cerium(IV) ammonium nitrate, $[Ce(NH_4)_2(NO_3)_6]$ (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**$^{\cdot+}$, but **3**$^{\cdot+}$ 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**$^{\cdot+}$ appears reasonable. In contrast, the 9,10-dicyanoanthracene (DCA)-sensitised electron-transfer photoreaction of $[^2H_4]$-**2** involved degenerate Cope rearrangement in which $[^2H_4]$-**3**$^{\cdot+}$ intervenes as an intermediate (Scheme 1).[3a–d] If the PET degenerate Cope is involved by the direct cleavage of $[^2H_4]$-**3**$^{\cdot+}$ in a cyclisation–cleavage mechanism, the reactivity of **3**$^{\cdot+}$ 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 $[^2H_4]$-**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 PET reaction of **1** afforded **2**, but no **4** at all. Upon irradiation ($\lambda > 410$ nm) of DCA with **1** in MeCN, CH_2Cl_2, and C_6H_6 under N_2 at ambient temperature, **2** was produced quantitatively. Because **1** [$E^{ox}_{1/2} = +1.16$ 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} dm^3 mol^{-1} s^{-1} in MeCN, CH_2Cl_2 and C_6H_6, respectively, and the free energy change (ΔG) for a single electron transfer (SET) from **1** to ^{1}DCA* was large and negative (-77 kJ mol^{-1}) in MeCN,§ PET to form **1**$^{\cdot+}$ 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 CH_2Cl_2 as shown in Table 1.



Scheme 1 The PET degenerate Cope rearrangement

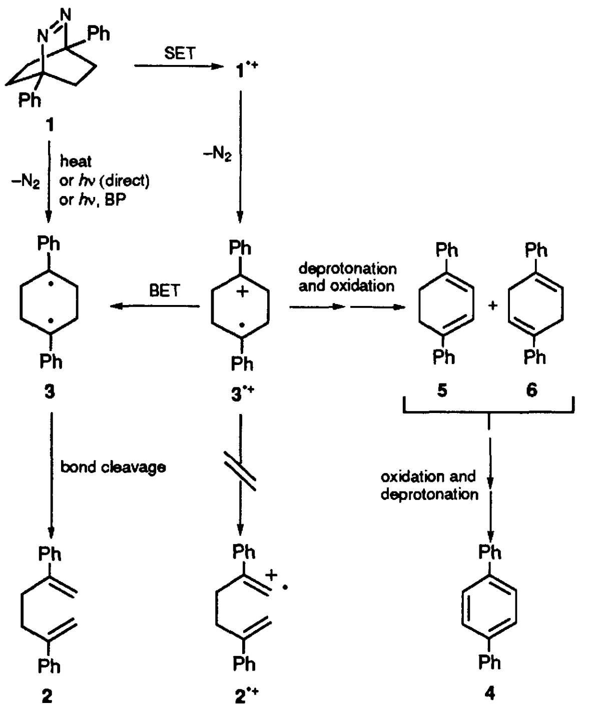
Deazetation reactions of **1** under PET conditions (entries 5–7) thus provided the same results as those under pyrolytic,[4a] direct irradiation[4b] and benzophenone (BP)-sensitised[4c] conditions (entries 8–10) where diyl **3** serves as a key intermediate, but are different from deazetations under non-PET conditions (entries 1–4). Because both PET and non-PET reactions of **1** are reasonably assumed to generate **3**$^{\cdot+}$ *via* **1**$^{\cdot+}$, 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**$^{\cdot+}$ 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 ($E^{ox}_{1/2} = +0.16$ V *vs.* SCE in MeCN)[6] and the electron acceptors ($E^{red}_{1/2} = -0.95$ 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**$^{\cdot+}$–acceptor$^{\cdot-}$] are calculated to be -107, -83 and 5.8 kJ mol^{-1}, respectively, for DCA, TCNB and TCNE. Cation radical **3**$^{\cdot+}$ generated under PET conditions thus suffers a rapid BET from DCA$^{\cdot-}$, TCNB$^{\cdot-}$ and TCNE$^{\cdot-}$ 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 $(4\text{-}BrC_6H_4)_3N$ to **3**$^{\cdot+}$ are highly endothermic as

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

Entry	Conditions	Solvent	Conv. (%)	Yields[a] (%) **2**	Yields[a] (%) **4**
1	CAN, $Bu^n_4NHSO_4$[b]	$CHCl_3$	100	0	46
2	CBN (1 equiv.)	CH_2Cl_2	55	0	18[c]
3	$(4\text{-}BrC_6H_4)_3N^{\cdot+}SbCl_6^-$ (2 equiv.)	CH_2Cl_2	40	0	29
4	Electrolysis (+1.25 V)	CH_2Cl_2	39	0	11
5	$h\nu_{sens}$ ($\lambda > 410$ nm), DCA	CH_2Cl_2	100	100	0
6	$h\nu_{CT}$ ($\lambda > 410$ nm), TCNB	CH_2Cl_2	100	100	0
7	$h\nu_{CT}$ ($\lambda > 410$ nm), TCNE	CH_2Cl_2	92	40	0
8	Heat[d] (110 °C)	PhMe	100	100	0
9	$h\nu$ (direct,[e] $\lambda > 320$ nm)	C_6H_6	100	100	0
10	$h\nu$ ($\lambda = 333$ nm), BP[f]	C_6H_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 [ΔG_{BET} = *ca.* 70 kJ mol^{-1} for Ce$^{\mathrm{III}}$ and 86 kJ mol^{-1} for (4-BrC$_6$H$_4$)$_3$N] indicate.[‡] Under non-PET conditions BET form **3** is thus unlikely, and **3**$^{\cdot+}$ is converted to **4** by successive deprotonation–oxidation steps[1] *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**$^{\cdot+}$ under PET conditions and further suggest the operation of the same process in the PET degenerate Cope rearrangement of [^{2}H$_4$]-**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 ($E^{\mathrm{red}}_{1/2}$ and $E^{\mathrm{ox}}_{1/2}$) were measured by cyclic voltammetry at a platinum electrode in dry MeCN with 0.1 mol dm^{-3} Et$_4$NClO$_4$ as a supporting electrolyte. The $E^{\mathrm{red}}_{1/2}$ values for CAN and CBN, and $E^{\mathrm{ox}}_{1/2}$ for (4-BrC$_6$H$_4$)$_3$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]: ΔG/kJ mol^{-1} = 96.5 [$E^{\mathrm{ox}}_{1/2}$ (**1**) − $E^{\mathrm{red}}_{1/2}$ (DCA) − $E_{0\text{–}0}$] − $e^2/\varepsilon r$, where $E^{\mathrm{ox}}_{1/2}$ (**1**) is +1.16 V *vs.* SCE, $E^{\mathrm{red}}_{1/2}$ (DCA) is −0.95 V, $E_{0\text{–}0}$ is 2.91 eV in MeCN and the coulombic term ($e^2/\varepsilon r$) 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 ^{1}H 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-diyl 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 diyl contribution to the PET reaction of **1** and the PET degenerate Cope rearrangement of [^{2}H$_4$]-**2**.

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