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Phenyl Substitution Effects on Rate Acceleration of Cation Radical Deazetation of 2,3-Diazabicyclo[2.2.2]oct-2-enes

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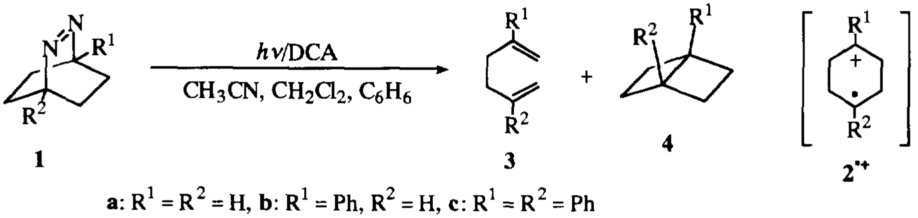
Abstract: *Under the 9,10-dicyanoanthracene (DCA)-photosensitized electron-transfer conditions 1-phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (**1b**) and 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene (**1c**) were deazetized with rate constants,* k_{-N_2}*, of ca.* 8.4×10^7 *and* 6.6×10^{10} s^{-1}*, respectively, whereas the parent 2,3-diazabicyclo[2.2.2]oct-2-ene (**1a**) was not reactive, showing remarkable rate acceleration by the* σ*(C-N)-*π *(Ph) orbital interaction due to the phenyl substitution.* Copyright © 1996 Elsevier Science Ltd

Recently, much attention has been focused on electron-transfer (ET) deazetations of 2,3-diazabicyclo-[2.2.2]oct-2-enes, potential precursors to cyclohexa-1,4-diyl cation radicals (CR) ($2^{\bullet+}$).[1-6] However, the deazetations were reported to depend strongly upon the ET conditions employed. Deazetation of the diphenyl derivative (**1c**) occurred facilely under both the DCA-sensitized and $Ce(NH_4)_2(NO_3)_6$ (CAN)-catalyzed ET conditions,[1,2] while the parent **1a** was deazetized neither by γ-ray irradiation in a Freon matrix,[3,4] tris(4-bromophenyl)aminium hexachloroantimonate-catalyzed reaction[5] nor by photoexcitation of the electron donor-acceptor (EDA) complex with tetracyanoethylene.[4] In addition, the deazetation product varied with change in the ET deazetation conditions. Diene **3c** was formed quantitatively from **1c** under the photoinduced electron-transfer (PET) conditions,[1] while the CAN-catalyzed reaction of **1c** gave 1,4-diphenyl-1,3-cyclohexadiene.[2] In order to gain mechanistic insight into deazetations of 2,3-diazabicyclo[2.2.2]oct-2-enes under ET conditions, we investigated phenyl substitution effects on rate acceleration of the DCA-sensitized CR deazetations of **1a-c** and found that the σ(C-N)-π(Ph) orbital interaction has significant impact on the deazetation efficiency.



a: $R^1 = R^2 = H$, **b**: $R^1 = Ph, R^2 = H$, **c**: $R^1 = R^2 = Ph$

In Table 1 are shown the Stern-Volmer ($k_q\tau$) and rate constants (k_q) for the DCA-fluorescence quenching by **1a-c** together with the halfwave oxidation potentials ($E^{ox}{}_{1/2}$)[7] of **1a-c** in CH_2Cl_2. In spite of large k_q close to the diffusion control rate, the DCA-sensitized photoreaction (λ > 410 nm) of **1a** in CD_3CN, CD_2Cl_2 or C_6D_6 resulted in a quantitative recovery either in the absence or presence of the cosensitizer biphenyl as well as the 2,4,6-triphenylpyrylium tetrafluoroborate-sensitized photoreaction of **1a**.[8]

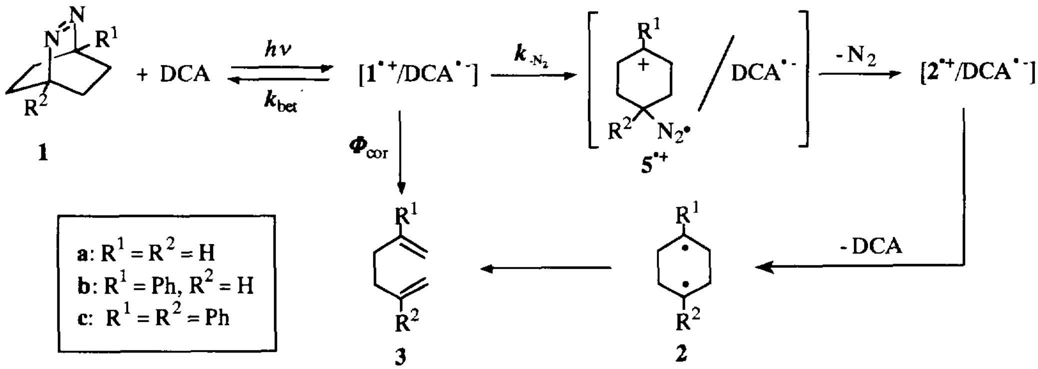
Table 1. Oxidation Potentials ($E^{ox}_{1/2}$) of **1a-c**, the Stern-Volmer ($k_q\tau$) and Rate Constants (k_q) for the DCA-Fluorescence Quenching, Observed Quantum Efficiencies (Φ) and Corrected Quantum Efficiencies (Φ_{cor}) for Deazetation and Calculated Rate Constants for BET (k_{bet}) and CR Deazetation (k_{-N_2}) in CH_2Cl_2

	$E^{ox}_{1/2}$ a)	$k_q\tau$	k_q	Φ b)	Φ_{cor}	k_{bet}	k_{-N_2}
	V	M^{-1}	$10^{10}\,M^{-1}\,s^{-1}$			$10^9\,s^{-1}$	$10^9\,s^{-1}$
1a	+1.66	127	1.09	0	0	0.94	~0
1b	+1.50	134	1.15	0.018	0.031	2.6	0.084
1c	+1.39	143	1.22	0.55	0.93	5.0	66

a) vs. SCE, scan rate 100 mV/s. b) [**1**] =0.01 M.

In contrast, the DCA-sensitized photoreactions of **1b** and **1c** in CH_2Cl_2 afforded 2-phenyl-1,5-hexadiene (**3b**) and **3c**, respectively, in quantitative yields.[8] Interestingly, the DCA-sensitized photoreaction of **1b** in benzene gave not only **3b** (67%) but also 1-phenylbicyclo[2.2.0]hexane (**4b**, 4%).[9] Similar results were obtained upon photoexcitation (λ > 410 nm) of the EDA complexes of **1b-c** and 1,2,4,5-tetracyanobenzene. The corrected quantum efficiencies (Φ_{cor}) for the formation of **3** were determined as $\Phi_{cor} = \Phi / Q_e$ by using observed quantum efficiencies (Φ)[10] and quenching efficiencies ($Q_e = k_q\tau[\mathbf{1}]/\{1 + k_q\tau[\mathbf{1}]\}$) (Table 1) and provided significant phenyl substitution effects on deazetation of **1**, showing that 93% of the ion pair [$\mathbf{1c}^{\bullet+}/DCA^{\bullet-}$] afforded **3c** whereas most of the ion pair [$\mathbf{1a}^{\bullet+}/DCA^{\bullet-}$] decayed to **1a** and DCA by back-electron transfer (BET).[11] In fact, nanosecond time-resolved laser flash photolysis of an aerated CH_2Cl_2 solution of **1b** and *N*-methylquinolinium tetrafluoroborate ($NMQ^+BF_4^-$) in the presence of 2 M toluene gave no transient absorption, whereas that of **1c** gave a transient absorption due to $\mathbf{2c}^{\bullet+}$ at λ_{max} = 482 nm, which was confirmed by comparison with absorption observed by similar laser flash photolysis of **3c** (Fig. 1).[12] Note that this λ_{max} is different from those of the free cumyl cation (326 nm, 390 nm)[13] and cumyl radical (315 nm),[14] suggesting the through-bond interaction between cation and radical counterparts. A plausible mechanism for the PET deazetation of **1** is shown in Scheme 1. Diazenyl and cyclohexa-1,4-diyl CRs ($\mathbf{5}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$) serve as key intermediates in a stepwise deazetation of $\mathbf{1}^{\bullet+}$. If this mechanism is really operative, Φ_{cor} can be further represented as $\Phi_{cor} = k_{-N_2} / (k_{-N_2} + k_{bet})$, in which k_{-N_2} and k_{bet} are rate constants of deazetation and BET in [$\mathbf{1}^{\bullet+}/DCA^{\bullet-}$]. By using calculated rate constants,[15] $k_{bet} = 2.6 \times 10^9$ and $5.0 \times 10^9\ s^{-1}$ for **1b** and **1c**, respectively, k_{-N_2} were estimated to be $8.4 \times 10^7\ s^{-1}$ for **1b** and $6.6 \times 10^{10}\ s^{-1}$ for **1c** as shown in Table 1. Thus, $\mathbf{1c}^{\bullet+}$

Scheme 1



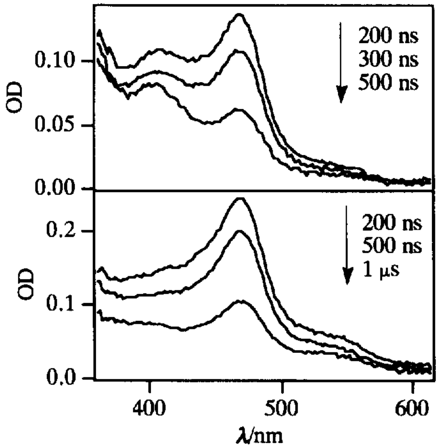


Fig. 1. Nanosecond absorption spectra of an aerated CH_2Cl_2 solutions of **1c** (1 mM, top) and **3c** (1 mM, bottom) under the $NMQ^+BF_4^-$ (1 mM)-toluene (2 M) cosensitized conditions.

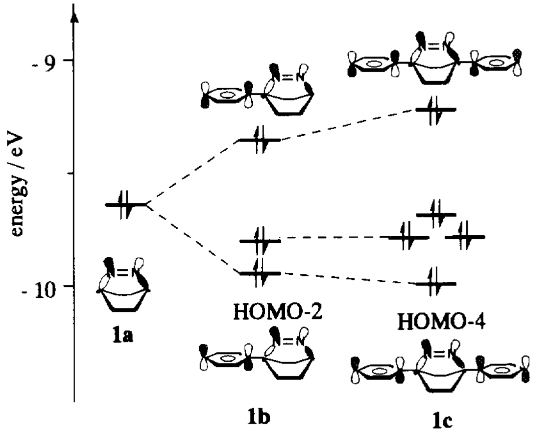


Fig. 2. Energy level diagram for occupied molecular orbitals of **1a-c** calculated by PM3.

undergoes deazetation *ca.* 800 times faster than **1b**$^{\bullet+}$. It is of interest to compare $k_{\text{-N}_2}$ of **1**$^{\bullet+}$ with rate constants of deazetation of the neutral counterparts. The calculated rate constants of thermal deazetations of **1a**, **1b** and **1c** were, respectively, 4.2×10^{-19}, 5.1×10^{-13} and 1.4×10^{-10} s^{-1} at 20 °C,[19] indicating that rate acceleration by the phenyl substitution is more significant in the CR state than the neutral state. It is also noteworthy that deazetations of **1b**$^{\bullet+}$ and **1c**$^{\bullet+}$ took place $>10^{20}$ times faster than those of the neutral counterparts.

One possible explanation for the phenyl substitution effects on CR deazetation is thermodynamics of the initial C-N bond cleavage of **1**$^{\bullet+}$ to **5**$^{\bullet+}$. The PM3/UHF calculations suggested that cleavage of **1a**$^{\bullet+}$ to **5a**$^{\bullet+}$ is 11.6 kcal/mol endothermic whereas that of **1b**$^{\bullet+}$ occurs with heat evolution of 6.9 kcal/mol.[20] Results of the calculation are in accord with conventional explanation in term of the difference in stability among secondary (**5a**$^{\bullet+}$) and tertiary (**5b**$^{\bullet+}$ and **5c**$^{\bullet+}$) CRs. Furthermore, the PM3 calculation revealed that HOMOs of **1b** and **1c** are comprised of an antibonding combination of HOMOs of **1a** and benzene, whereas their bonding combinations form the third HOMO of **1b** (HOMO-2 in Fig. 2) and the fifth HOMO of **1c** (HOMO-4). The latter combination is due to the σ(C-N)-π (Ph) orbital interaction, which can diminish the C-N bond order just as hyperconjugation does. A similar but more efficient σ (C-N)-π (Ph) orbital interaction is apparently available for **1b**$^{\bullet+}$ and **1c**$^{\bullet+}$, because upon loss of an electron from HOMOs, the HOMO-2 of **1b**$^{\bullet+}$ and HOMO-4 of **1c**$^{\bullet+}$ increase in contribution to total MOs as compared with neutral **1b** and **1c**. Therefore, the more effective rate acceleration by the phenyl substitution in the CR state than the neutral state must be attributed to the more efficient σ (C-N)-π (Ph) orbital interaction.

In conclusion, the observed remarkable rate acceleration for CR deazetations of 2,3-diazabicyclo-[2.2.2]oct-2-enes can be accounted for by the σ (C-N)-π (Ph) orbital interaction due to the phenyl substitution which consequently involves exothermic initial C-N bond cleavage.

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7. $E^{\mathrm{ox}}_{1/2}$ were estimated as E_{pa} (anodic peak potentials) - 0.03 V, which were measured by cyclic voltammetry at a platinum electrode in dry CH_2Cl_2 with 0.1 M *n*-Bu_4NBF_4 as a supporting electrolyte.
8. A 0.5 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter ($\lambda > 410$ nm) at 20 °C.
9. Selected data of **4b**.: Colorless oil. Anal; Calcd. for $C_{12}H_{14}$; C = 91.08%, H = 8.92%. Obsd.; C = 88.16%, H = 8.71%. HRMS (EI, 70 eV); Calcd. for $C_{12}H_{14}$; 158.1095. Obsd.; 158.1098. MS (70 eV, *m/z*, %); 158 (M^+, 13), 143 (8), 130 (32), 129 (35), 115 (100), 104 (39), 91 (38), 77 (45). IR (neat, cm^{-1}); 2920, 1600, 1496, 757, 696. ^1H NMR (200 MHz, $CDCl_3$); δ_{ppm} 1.95 - 2.14 (m, 2 H), 2.33 - 2.64 (m, 6 H), 2.93 - 3.07 (m, 1 H), 7.10 - 7.39 (m, 5 H). ^{13}C NMR (50 MHz, $CDCl_3$); δ_{ppm} 24.97 (2 C), 34.56 (2 C), 40.30, 49.11, 124.68 (2 C), 125.28, 128.19 (2 C), 148.68.
10. A 3 mL CH_2Cl_2 solution was irradiated ($\lambda = 436 \pm 12$ nm) at 20 °C with a 500 W Hg-Xe lamp through a cutoff filter ($\lambda > 350$ nm), an interference filter ($\lambda_{\max} = 437$ nm), and an aqueous $CuSO_4$ solution filter. [**1**] = 0.01 M, [DCA] = 1.38×10^{-3} M. Aberchrome 540 was used as an actinometer.
11. Kitamura and coworkers pointed out the importance of BET in CR deazetations: (*a*) Karatsu, T.; Itoh, H.; Kikunaga, T.; Ebashi, Y.; Hotta, H.; Kitamura, A. *J. Org. Chem.,* **1995,** *60*, 8270-8277. (*b*) Karatsu, T.; Ichino, Y.; Kitamura, A.; Owens, W. H.; Engel, P. S. *J. Chem. Res. (S),* **1995**, 440-441.
12. An excimer laser ($\lambda_{\mathrm{ex}} = 308$ nm) was used for nanosecond absorption spectrometry. A similar deazetation of **1c** took place in CH_2Cl_2 under the $NMQ^+BF_4^-$-toluene cosensitized conditions ($\lambda = 305 \pm 5$ nm).
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15. The calculated rate constants, k_{bet}, were obtained from the following equations (1, 2)[16] by using reported parameters in CH_2Cl_2.[17, 18]

$$k_{\mathrm{bet}} = \left(\frac{4\pi^3}{h^2\lambda_s k_b T}\right)^{1/2}|V|^2\sum_{\omega=0}^{\infty}\left(\frac{e^{-s}S^{\omega}}{\omega!}\right)\exp\left\{-\frac{(\lambda_s + \Delta G + \omega h\nu)^2}{4\lambda_s k_b T}\right\} \quad (1), \qquad S = \lambda_v / h\nu \quad (2)$$

16. (*a*) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.,* **1984**, *106*, 5057-5068. (*b*) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.,* **1981**, *103*, 741-747, 748-752. (*c*) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974,** *5*, 183-197. (*d*) Ulstrup, J.; Jortner, J. *J. Chem. Phys.,* **1975,** *63*, 4358-4368.
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18. The ΔG_{bet} values for BET in $[\mathbf{1}^{\bullet+}/\mathrm{DCA}^{\bullet-}]$ in CH_2Cl_2 were estimated by the following equations: $\Delta G_{\mathrm{bet}} = -\{E^{\mathrm{ox}}_{1/2}(\mathbf{1}) - E^{\mathrm{red}}_{1/2}(\mathrm{DCA}) - e^2/\varepsilon r\}$, where $E^{\mathrm{red}}_{1/2}(\mathrm{DCA}) = -0.89$ V and $e^2/\varepsilon r = 0.23$ eV.
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20. PM3 calculations were carried out by using the MOPAC ver. 6 on a Tektronix CAChe WorkSystem.

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