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Photoinduced Electron-Transfer Bicyclopropenyl-benzene Rearrangements of 2,2′,3,3′-Tetraphenylbicyclopropenyls: A New Mechanism via Dewar Benzene

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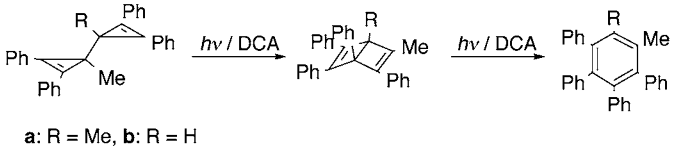
ABSTRACT



The 9,10-dicyanoanthracene-sensitized photoreaction of 1-methyl- and 1,1′-dimethyl-2,2′,3,3′-tetraphenylbicyclopropenyl gives the corresponding benzene and Dewar benzene derivatives, indicating that their photoinduced electron-transfer bicyclopropenyl-benzene rearrangements proceed via Dewar benzenes.

According to theoretical calculations,[1] bicyclopropenyl is the highest in energy among all valence isomers of benzene. Since the pioneering work of Breslow[2a] first demonstrated that, on heating, hexaphenylbicyclopropenyl underwent isomerizatoin to give hexaphenylbenzene, several reaction mechanisms were proposed for the bicyclopropenyl-benzene rearrangements, which were achieved by thermolyses,[2] Ag^+-catalyzed reactions,[3] and photolyses.[4] The rearrangement can be also triggered by photoinduced electron transfer (PET). A CIDNP study[5] of the *p*-chloranil-sensitized photoreaction of 1,1′-dimethylbicyclopropenyl (**1**) revealed that the initially formed tricyclohexane radical cation $\mathbf{2}^{\bullet +}$ rearranges to dimethylbenzvalene radical cations, which, in turn, rearrange to *o*- and *m*-xylenes. The 9,10-dicyanoanthracene (DCA)-sensitized photoreaction of 1,1′-dimethyl-2,2′,3,3′-tetraphenylbicyclopropenyl (**3a**) in acetonitrile was reported[6] to form 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (**4a**) exclusively via a tricyclohexane radical cation intermediate $\mathbf{5a}^{\bullet +}$. To gain further insight into the mechanistic pathway[7] for **3**, we reinvestigated the DCA-sensitized photoreactions of **3a** as well as 1-methyl-2,2′,3,3′-tetraphenylbicyclopropenyl (**3b**).[2c] Here, we report that the intrinsic process is the formation of

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(2) Thermolyses: (a) Breslow, R.; Gal, P. *J. Am. Chem. Soc.* **1959**, *81*, 4747−4748. (b) Breslow, R.; Gal, P.; Chang, H. W.; Altman, L. J. *J. Am. Chem. Soc.* **1965**, *87*, 5139−5144. (c) Weiss, R.; Köbl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3224−3225. (d) Turro, N. J.; Schuster, G. B.; Bergman, R. G.; Shea, K. J.; Davis, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 4758−4760. (e) Davis, J. H.; Shea, K. J.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 232−234; *Angew. Chem.* **1976**, *88*, 254−255. (f) Davis, J. H.; Shea, K. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1499−1507. See also refs 3b,c.

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(4) Photolyses: Weiss, R.; Köbl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3222−3224. See also refs 2a,b.

(5) Abelt, C. J.; Roth, H. D. *J. Am. Chem. Soc.* **1985**, *107*, 3840−3843.

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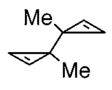
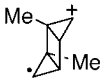
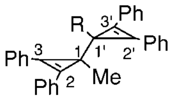
10.1021/ol049917j CCC: $27.50



1

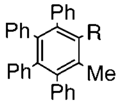


2$^{\bullet+}$



3

a: R = Me, **b**: R = H



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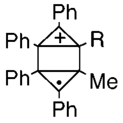
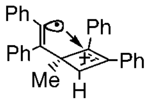
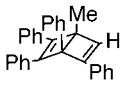


5$^{\bullet+}$



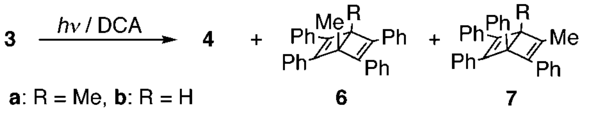
9b$^{\bullet+}$



10b

two types of Dewar benzenes[9] **6** and **7** (Scheme 1), which cannot be accounted for by a tricyclohexane radical cation intermediate like **5**$^{\bullet+}$.

Scheme 1. DCA-Sensitized PET Reaction of **3**



The anodic peak oxidation potentials (E_{pa})[10] of **3a** (+1.24 V vs SCE in dichloromethane) and **3b** (+1.22 V) are low enough to quench the excited singlet state of DCA exergonically, as suggested by their respective calculated free energy changes for electron transfer,[11] $\Delta G_{et} = -1.00$ and -1.02 eV, in dichloromethane. In agreement with the estimate, **3a** and **3b** quench the fluorescence of DCA efficiently with respective rate constants of $k_q = 1.9$ and 1.8×10^{10} M^{-1} s^{-1} in dichloromethane.

The DCA-sensitized photoreactions of **3a** ($\lambda > 410$ nm) in degassed dichloromethane-d_2 at 20 °C differ from previously reported results[6] in acetonitrile. As shown in Scheme 1, Dewar benzenes[9] **6a** and **7a** are formed together with **4a** in a product ratio that significantly depends on irradiation time. At 86% conversion (10 h), **4a**, **6a**, and **7a** are formed in 46, 24, and 14% yields, respectively, but prolonged irradiation (30 h) results in the formation of a mixture of **4a** (72%) and **6a** (28%).[14] The fact that the yield of **4a** increases while that of **7a** decreases and that of **6a** does not change suggests that **7a** readily rearranges to **4a**, while **6a** is stable under the conditions employed. Similarly, the DCA-sensitized photoreaction of **3b** in dichloromethane-d_2 at 20 °C gives **4b** (>+2.0 V), **6b**[3b] (+1.48 V), and **7b** (+1.38 V) in 35, 18, and 41% yields, respectively, at 94% conversion of **3b**. Figure 1 shows the time-dependent changes of the product ratios observed during irradiation, suggesting that the immediate precursor of **4b** is Dewar benzene **7b**. Actually, the independent PET reactions of **6b** and **7b** result in the quantitative recovery of **6b** and formation of **4b**, respectively. Note that **7b** rearranges to **4b** slowly, even at 20 °C in the dark. Therefore, the formation of Dewar benzenes **6** and **7** excludes the intermediacy of the tricyclohexane radical cation **5**$^{\bullet+}$.

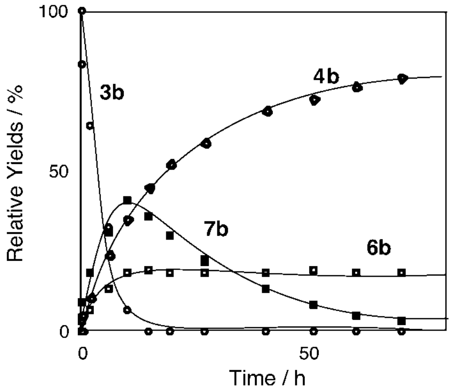
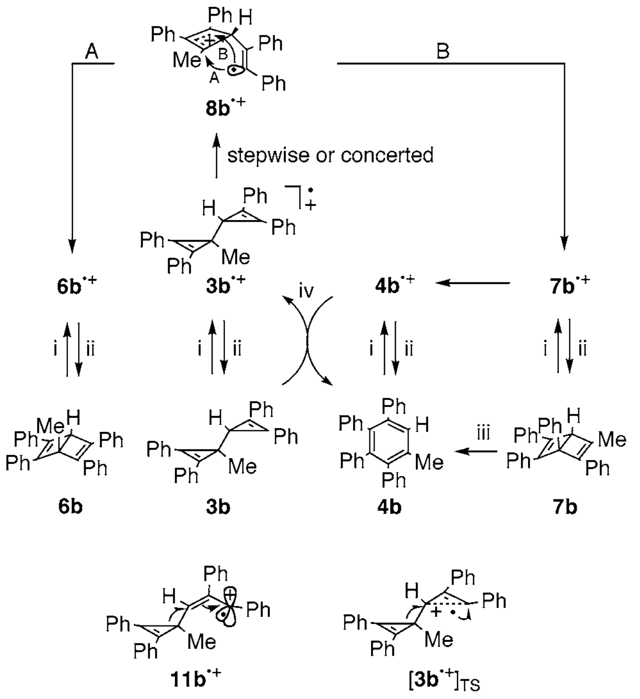


Figure 1. Time-dependent changes in the product ratios in the DCA-sensitized PET reaction of **3b** (0.1 M) in degassed dichloromethane-d_2 at 20 °C. The product yields were determined using ^{1}H NMR. The material balance is 100%.

A plausible mechanism for formation of **3b** via Dewar benzene derivatives is depicted in Scheme 2. The ring cleavage of the cyclopropene C$_1'$−C$_2'$ (or C$_1'$−C$_3'$) bond

Scheme 2. Plausible Mechanism for the PET Bicyclopropenyl-benzene Rearrangement of **3b**[a]



[a] Conditions: (i) hν/DCA, (ii) back-electron-transfer from DCA$^{\bullet-}$, (iii) Δ at 20 °C, (iv) hole transfer.

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(7) The real structures of Dewar benzene derivatives and their mechanism of formation in the electron-transfer reactions of bicyclopropenyl or cyclopropenyl cation remain controversial. See ref 8.

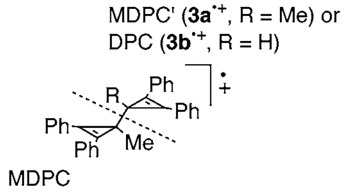
(8) Komatsu, K.; Kitagawa, T. *Chem. Rev.* **2003**, *103*, 1371−1427.

(9) Weiss and co-workers were the first to isolate Dewar benzene derivatives and demonstrated their contribution in thermal, Ag$^+$-catalyzed, and photolytic bicyclopropenyl-benzene rearrangements. See refs 2c, 3a−c, and 4.

associated with the ring expansion of the other cyclopropene ring of $\mathbf{3b}^{\bullet+}$ forms a σ radical-allyl cation intermediate $\mathbf{8b}^{\bullet+}$. Whether this Wagner−Meerwein-type rearrangement occurs stepwise[15] via an intermediate $\mathbf{11b}^{\bullet+}$ or concertedly via the transition state $[\mathbf{3b}^{\bullet+}]_{TS}$, the two-bond cleavage process to form $\mathbf{8b}^{\bullet+}$ is essentially the same as those in the Ag^+-catalyzed reactions and thermolyses of bicyclopropenyls proposed by Weiss[3b,c,9] and Bergman.[2e,f] Dewar benzene **6b** is formed via the ring closure A in $\mathbf{8b}^{\bullet+}$ to $\mathbf{6b}^{\bullet+}$ followed by back electron transfer (BET) from $DCA^{\bullet-}$. Radical cation $\mathbf{7b}^{\bullet+}$ formed by competitive ring closure B rearranges to $\mathbf{4b}^{\bullet+}$. Products **7b** and **4b** are formed after BET in $\mathbf{7b}^{\bullet+}$ and $\mathbf{4b}^{\bullet+}$, respectively. Dewar benzene **7b** with the phenyl group at the sp^3 carbon rearranges readily to **4b** under the PET conditions employed.

Radical cation $\mathbf{3b}^{\bullet+}$ can form formally alternative σ radical-allyl cation $\mathbf{9b}^{\bullet+}$, which would give **6b**, **4b**, and the unobserved Dewar benzene **10b**. Because **10b** with the phenyl and methyl groups at the sp^3 carbons would be probably more unstable than **7b** under the condition employed, the fact that **10b** is not found during the reaction does not necessarily indicate that $\mathbf{9b}^{\bullet+}$ is not involved with the reaction of **3b**. However, a preferential formation of $\mathbf{8b}^{\bullet+}$ over $\mathbf{9b}^{\bullet+}$ is expected from the point of view of thermodynamic stability: $\mathbf{8b}^{\bullet+}$ with a *tertiary* allylic cation is more stable than $\mathbf{9b}^{\bullet+}$ containing a *secondary* allylic cation.

The formation of **6b** and **7b** from the unsymmetrical bicyclopropenyl **3b** apparently requires the regiospecific $C_1'-C_2'$ (or $C_1'-C_3'$) cleavage of $\mathbf{3b}^{\bullet+}$, in which the unpaired electron and positive charge are predominantly localized on the diphenylcyclopropyl (DPC) subunit, the cyclopropene ring without a methyl group (Figure 2). To gain further insight into the electronic structure of $\mathbf{3a}^{\bullet+}$ and $\mathbf{3b}^{\bullet+}$, we conducted semiempirical and DFT calculations.[17,22]



$\mathbf{3}^{\bullet+}$

Figure 2. Definition of two subunits in $\mathbf{3}^{\bullet+}$.

Table 1. Sum of the Calculated Partial Spin (ρ) and Charge (q) Densities of $\mathbf{3a}^{\bullet+}$ (C_{2h}) and $\mathbf{3b}^{\bullet+}$ (C_s)

		MDPC		MDPC′ or DPC	
		$\Sigma\rho$	Σq	$\Sigma\rho$	Σq
$\mathbf{3a}^{\bullet+}$	AM1/ROHF	+0.50	+0.50	+0.50	+0.50
	AM1/UHF	+0.50	+0.50	+0.50	+0.50
	PM3/UHF	+0.50	+0.50	+0.50	+0.50
	ROB3LYP/6-31G(p)	+0.50	+0.50	+0.50	+0.50
$\mathbf{3b}^{\bullet+}$	AM1/ROHF	+0.12	+0.17	+0.88	+0.83
	AM1/UHF	+0.05	+0.12	+0.95	+0.88
	PM3/UHF	+0.05	+0.11	+0.95	+0.89
	ROB3LYP/6-31G(p)	+0.06	+0.17	+0.94	+0.83

Table 1 shows the sum of the calculated partial spin and charge density, $\Sigma\rho$ and Σq, respectively, for two methyl-diphenylcyclopropyl (MDPC) subunits of $\mathbf{3a}^{\bullet+}$ and for the MDPC and DPC subunits in $\mathbf{3b}^{\bullet+}$. Both $\Sigma\rho$ and Σq values for the MDPC subunit of $\mathbf{3a}^{\bullet+}$ are +0.50, regardless of the method of calculation. Those for another MDPC subunit (MDPC′) are accordingly +0.50. In sharp contrast, an unsymmetrical electronic structure is suggested for $\mathbf{3b}^{\bullet+}$. The $\Sigma\rho$ and Σq values for the DPC subunits of $\mathbf{3b}^{\bullet+}$ are +0.88∼0.95 and +0.83∼0.89, respectively: the residual spin and charge are suggested to locate in the MDPC subunit. Results of the calculation indicate that the unpaired electron and positive charge of $\mathbf{3b}^{\bullet+}$ are delocalized predominantly on the DPC, the less electron-donating subunit, while they are distributed evenly over two MDPC subunits of $\mathbf{3a}^{\bullet+}$. Figure 3 represents contrasting SOMOs of $\mathbf{3a}^{\bullet+}$ and $\mathbf{3b}^{\bullet+}$ calculated by ROB3LYP/6-31G(p). Thus, the semiempirical and DFT calculations support the characteristic electronic structure of $\mathbf{3b}^{\bullet+}$. If this estimate is appropriate, the fact that the isomeric Dewar benzene **10b** expected from the alternative radical cation intermediate $\mathbf{9b}^{\bullet+}$ is not observed during

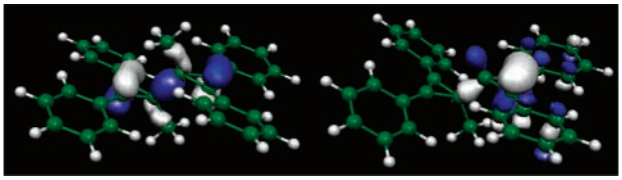


Figure 3. Representation of the SOMOs of $\mathbf{3a}^{\bullet+}$ (left, C_{2h}) and $\mathbf{3b}^{\bullet+}$ (right, C_s) calculated by ROB3LYP/6-31G(p).

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(10) Values of E_{pa} were measured by cyclic voltammetry (Pt electrode, scan rate 100 mV/s) in dry dichloromethane with 0.1 M n-$Bu_4N^+BF_4^-$ as a supporting electrolyte. All substrates gave irreversible waves.

(11) Values of ΔG_{et} were estimated by using the Rehm−Weller equation:[12] $\Delta G_{et} = E^{ox}_{1/2}(\mathbf{3}) - E^{red}_{1/2}(DCA) - E_{0-0}(DCA) - e^2/\epsilon r$, where $E^{red}_{1/2}(DCA) = -0.89$ V,[13] $E_{0-0}(DCA) = 2.87$ eV, and $e^2/\epsilon r = 0.23$ eV in dichloromethane. The halfwave oxidation potentials ($E^{ox}_{1/2}$) were obtained as $E_{pa} - 0.03$ V, assuming a one-electron oxidation process.

(12) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271.

(13) Ikeda, H.; Minegishi, T.; Takahashi, Y.; Miyashi, T. *Tetrahedron Lett.* **1996**, *37*, 4377−4380.

(14) We observed also that a similar photoreaction (1.5 h) of **3a** in acetonitrile at 20 °C gave **4a** and **6a** in 83 and 17% yields, respectively.

(15) For the bond cleavage of cyclopropene radical cations, see ref 16.

(16) Padwa, A.; Chou, C. S.; Rieker, W. F. *J. Org. Chem.* **1980**, *45*, 4555−4564.

(17) Semiempirical and DFT calculation was carried out at C_{2h} ($\mathbf{3a}^{\bullet+}$) or C_s ($\mathbf{3b}^{\bullet+}$) symmetry using PC GAMESS ver. 6.3,[18] WinMOPAC2002,[19] and Gaussian98[20] softwares. Figure 3 was drawn using MOLEKEL software.[21]

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(19) *MOPAC2002*; Stewart, J. J. P. Fujitsu, Ltd.: Tokyo, Japan, 2002.

irradiation is not inconsistent with the unique electronic structure of **3b**$^{\bullet+}$. According to orbital interaction theory,[24] the characteristic electronic structure of **3b**$^{\bullet+}$ is probably due to the electronic coupling of two cyclopropene rings through space and through two C−C σ-bonds ($C_1'-C_1-Me$). Similar electronic couplings were suggested by theoretical calculations for the neutral forms of the parent bicyclopropenyl and related compounds.[25]

The high efficiency of the PET reaction is another feature of **3b**. The corrected quantum efficiency (Φ_c)[26] per ion radical pair [**3b**$^{\bullet+}$/DCA$^{\bullet-}$] for the formation of **4b**, **6b**, and **7b** at a 10 mM concentration of **3b** is 1.4, indicating a chain mechanism for the photoreaction of **3b**. The hole transfer (HT) from **4b**$^{\bullet+}$ to **3b** with a negative free energy change ($\Delta G_{ht} < -0.81$ eV) is a key process. If the rate of HT (k_{ht}) is close to the diffusion control rate (2.2×10^{10} M^{-1} s^{-1} at 20 °C), the pseudo-first-order rate constant (k_{ht}[**3b**]) at the initial stage is calculated to be 2.2×10^8 s^{-1}, which is faster than $k_{bet} < 7.6 \times 10^7$ s^{-1} for the BET[27] from DCA$^{\bullet-}$ to **4b**$^{\bullet+}$. Thus, **4b**$^{\bullet+}$ acts as a carrier and undergoes HT much faster than **6b**$^{\bullet+}$ and **7b**$^{\bullet+}$, which suffer BET[30] from DCA$^{\bullet-}$ much faster than **4b**$^{\bullet+}$. Interestingly, similar thermodynamics and kinetics are expected for **4a**$^{\bullet+}$, but the Φ_c of **3a** is as low as 0.13. The remarkable difference in Φ_c between **3a** and **3b** is probably due to the extreme distribution of the unpaired electron and positive charge in **3b**$^{\bullet+}$, which facilitates the Wagner−Meerwein-type rearrangement of **3b**$^{\bullet+}$ to **8b**$^{\bullet+}$.

In conclusion, our experimental results first demonstrate a new mechanism via Dewar benzene for the PET bicyclopropenyl-benzene rearrangements of tetraphenyl-substituted bicyclopropenyl derivatives. This is in line with the mechanisms proposed by Weiss and Bergman for the Ag$^+$-catalyzed reactions and thermolyses. Consequently, this work proposes a topologically common reaction pathway via Dewar benzene that is applicable to thermolyses, Ag$^+$-catalyzed reactions, and PET reactions of tetraphenyl-substituted bicyclopropenyl derivatives.

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Supporting Information Available: Experimental details including physical data for **6** and **7** and Cartesian coordinates and $\Sigma\rho$ and Σq values for **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$ (ROB3LYP/6-31G(p)). This material is available free of charge via the Internet at http://pubs.acs.org.

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[27] Rate constant (k_{bet}) for the BET from DCA$^{\bullet-}$ to **4b**$^{\bullet+}$ at 20 °C in dichloromethane was calculated using the following equations (1,[28] 2,[28] and 3) and parameters reported by Kikuchi and co-workers:[29]

$$k_{bet} = \left(\frac{4\pi^3}{h^2\lambda_s k_b T}\right)^{1/2} |V|^2 \sum_{w=0}^{\infty}\left(\frac{e^{-S}S^w}{W!}\right)\exp\left\{-\frac{(\lambda_s + \Delta G_{bet} + wh\nu)^2}{4\lambda_s k_b T}\right\} \quad (1)$$

$$S = \lambda_v/h\nu \quad (2)$$

$$\Delta G_{bet} = -[E^{ox}{}_{1/2}(\mathbf{4b}) - E^{red}{}_{1/2}(\mathrm{DCA}) - e^2/\epsilon r] \quad (3)$$

where parameters V, λ_s, λ_v, ν, and ΔG_{bet} are, respectively, the electronic coupling matrix element (18 cm^{-1}), solvent reorganization energy (1.0 eV), vibration reorganization energy (0.3 eV), single average frequency (1500 cm^{-1}), and free energy change for electron-transfer process. In addition, h, k_b, and T, are Planck's constant, Boltzmann's constant, and the temperature (293 K), respectively.

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[30] Values of k_{bet} for the BET from DCA$^{\bullet-}$ to **6b**$^{\bullet+}$ and **7b**$^{\bullet+}$ were calculated to be 3.5 and 6.2×10^9 s^{-1}, respectively.