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Electrocycloreversion of Benzocyclobutenols Promoted by Photoinduced Electron Transfer

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Abstract: Benzocyclobutenols **1** undergo electron-transfer induced electrocycloreversion to generate *o-quinodimethane* intermediates *E*-**4** and *Z*-**4**, which then tautomerize to benzophenones **2**. Evidence for the intermediates is provided by the trapping experiments and the laser flash photolysis experiments.
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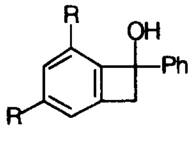
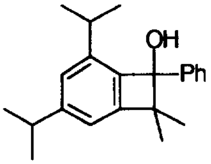
Thermally induced electrocycloreversion of cyclobutenes and benzocyclobutenes is well known and numerous examples have been reported.[1,2] On the other hand, the number of examples for the corresponding reactions of cation radicals is very limited although there has been growing interest in the cation radical reactions.[3—7] Photoinduced electron transfer (PET) is a powerful means whereby such reactions can be investigated. Indeed, photoexcitation of electron donor-acceptor (EDA) complexes and ET photosensitization have been employed to probe the reactivity of cyclobutenes and benzocyclobutenes in the cation radical manifold.[7] We have investigated the PET reactions of benzocyclobutenols **1a—c** and found that their cycloreversion can be promoted by PET.

1,2,4,5-Tetracyanobenzene (TCNB) forms the EDA complexes with **1a** and **1b** in dichloromethane. Although their CT-absorption maxima were obscured by the absorption of TCNB tailing up to *ca.* 340 nm, their absorption bands had sizable intensities in the wavelength region from 340 to 410 nm, sufficient to carry out photoexcitation. The photolyses were performed by irradiation ($\lambda > 350$ nm) using a 2 kW xenon lamp. The results are summarized in Table 1. Irradiation of a solution of **1a** and TCNB in dichloromethane for 1 h afforded 2-methylbenzophenone **2a** (13%) and compound **3a** (25%) with recovery of **1a** in 62% yield (Table 1, Run 1). Similar photoreaction with **1b** resulted in the formation of 2,4,6-trimethylbenzophenone **2b** (46%) and **3b** (36%) (Run 4). Products **2** were identified by spectral comparison with the authentic samples and the structure of **3** was determined by the spectral data.[8]

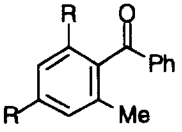
Photosensitization using 2,6,9,10-tetracyanoanthracene (TeCA) was also found to be effective for the isomerization of **1** to **2**. Benzocyclobutenols **1a—c** are relatively good electron donors to quench the fluorescence of TeCA.[9] The quenching rate constants were determined to be 9.6×10^{9}, 1.4×10^{10}, and 6.7×10^{9} M^{-1} s^{-1} in dichloromethane, respectively. The TeCA-sensitized photolyses were also performed in nitrogen-saturated dichloromethane solution by irradiation using a 2 kW xenon lamp ($\lambda > 400$ nm). Photoreaction of **1a**



1a: R = H
1b: R = Me



1c



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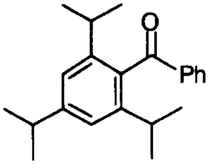
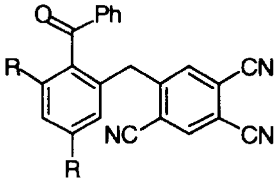
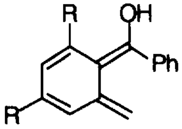


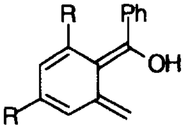
2c



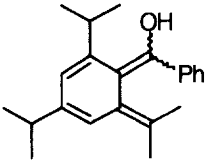
3a: R = H
3b: R = Me



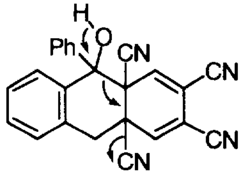
E-**4a**: R = H
E-**4b**: R = Me



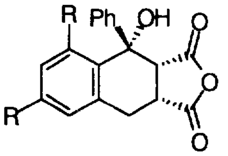
Z-**4a**: R = H
Z-**4b**: R = Me



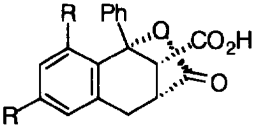
E-**4c**
Z-**4c**



5a: R = H
5b: R = Me



6a: R = H
6b: R = Me



7a: R = H
7b: R = Me

Table 1. Photoinduced electron transfer reactions of **1**

Run	Substrate	Acceptor	Additive	Irrad. time	Products (%)	Recovery (%)
1	**1a**	TCNB	None	1 h	**2a** (13), **3a** (25)	62
2	**1a**	TCNB	MA (0.06 mmol)	1 h	**2a** (7), **6a** (10)	83
3	**1a**	TCNB	MA (0.6 mmol)	3 h	**2a** (11), **6a** (22)	55
4	**1b**	TCNB	None	1 h	**2b** (46), **3b** (36)	0
5	**1b**	TCNB	MA (0.06 mmol)	1 h	**2b** (12), **6b** (10)	57
6	**1b**	TCNB	MA (0.6 mmol)	1 h	**2b** (13), **6b** (16)	43
7	**1a**	TeCA	None	20 min	**2a** (99)	0
8	**1a**	TeCA	MA (0.1 mmol)	20 min	**2a** (33), **6a** (67)	0
9	**1a**	TeCA	MA (1.0 mmol)	20 min	**2a** (32), **6a** (62)	0
10	**1b**	TeCA	None	20 min	**2b** (99)	0
11	**1b**	TeCA	MA (0.1 mmol)	20 min	**2b** (40), **6b** (43)	0
12	**1b**	TeCA	MA (1.0 mmol)	20 min	**2b** (47), **6b** (34)	0
13	**1c**	TeCA	None	30 min	**2c** (58)	27
14	**1c**	TeCA	MA (1.0 mmol)	30 min	**2c** (59)	9

The photolyses were performed by using a 2 kW xenon lamp. For the CT-irradiations, solutions of **1** (0.15 mmol) and TCNB (0.075 mmol) in dichloromethane (3 ml) were used. For the phorosensitizations, solutions of **1** (0.10 mmol) and TeCA (0.002 mmol) in dichloromethane (5 ml) were used. Yields are based on ^{1}H-NMR (200 MHz) analyses.

and **1b** under the above conditions afforded benzophenone **2a** and **2b** almost quantitatively (Run 7, 10). Similar photosensitized reactions of **1c** also resulted in the isomerization to give **2c** in 58% yield with 27% recovery of **1c** (Run 13). Photosensitization using 9,10-dicyanoanthracene was also found to be effective for conversion of **1** to **2**. However, the efficiency, particularly in the case of **1a**, was much lower compared to the TeCA-sensitization. 9-Cyanoanthracene or 9-phenylanthracene did not sensitize the reaction.

These results suggest that the electrocycloreversion of **1** can be promoted by PET. It is conceivable that cation radicals $\mathbf{1}^{\bullet+}$ in photogenerated ion pairs [$\mathbf{1}^{\bullet+}$, $\mathrm{Acc}^{\bullet-}$] undergo ring opening to give E-$\mathbf{4}^{\bullet+}$ and Z-$\mathbf{4}^{\bullet+}$ and then back electron transfer from the acceptor anion radicals ($\mathrm{Acc}^{\bullet-}$) occurs to generate *o*-quinodimethanes *E*-**4** and *Z*-**4** as precursors to **2**. Such intermediates of *E* and *Z* configurations are often referred to as "photoenols" since they can be generated by photolysis of 2-methylphenyl ketone derivatives.[10] While *Z*-isomers rapidly isomerize back to the starting ketones, the corresponding tautomerization of *E*-isomers is much slower and thus they are long-lived. In this respect, the most likely pathway for the formation of compound **3** is to involve the [4 + 2] cycloaddition reaction of *E*-**4** with TCNB leading to adducts **5**, which is then followed by loss of HCN.

In order to gain insight into the intermediacy of **4**, trapping experiments with maleic anhydride (MA) were examined. Thus, photoirradiation of the **1a**— and **1b**—TCNB systems in the presence of MA resulted in MA adducts **6a** and **6b** instead of **3a** and **3b** with concomitant formation of **2a** and **2b** (Run 2, 3, 5, 6). Adducts **6a** and **6b** could be converted to acid lactones **7a**[11] and **7b** in refluxing toluene, which establishes their stereochemistry as *cis* with respect to the hydroxy and the carbonyl groups. Photosensitization of **1a** and **1b** with TeCA in the presence of MA also led to the formation of **6a** and **6b** with concomitant formation of **2a** and **2b** (Run 8, 9, 11, 12). In the case of **1c**, no formation of the MA adduct was observed, but ketone **2c** was obtained in 59% yield. We presume that this is due to the lower reactivity of *E*-**4c** toward dienophiles owing to the expected steric effects of the two extra methyl groups on the exo methylene.

A preliminary laser flash photolysis experiment with the **1a**—TCNB system in dichloromethane provided additional insight into the reaction mechanism. Pulsed laser excitation (Nd: YAG, 355 nm) of the CT band of the **1a**—TCNB complex generated a transient species absorbing at λ_{max} 395 nm, whose decay profile was biphasic with fast first-order process (k = 1.2 × 10^7 s^{-1}) followed by much slower first-order process (k = *ca.* 10^3 s^{-1}).[12] We assign the shorter lived transients as being due to *Z*-**4a** and the longer lived species to *E*-**4a**. The rate constant of the short-lived species is comparable with the reported value of 2.0 × 10^7 s^{-1} for *Z*-**4a** in cyclohexane.[13] The decay rate of the long-lived species became faster with increased concentration of the added MA, which is consistent with the results of the trapping experiment and supports the assignment. The rate constant (k_{add}) for the addition of MA to *E*-**4a** was evaluated to be 2.2 × 10^6 M^{-1} s^{-1} at 25 °C from a plot of the decay rates *vs.* the concentration of the added MA. No other transients ascribable to ion pairs or free ions could be detected in the flash photolysis experiment, suggesting that cation radical $\mathbf{1a}^{\bullet+}$ in a photogenerated ion pair [$\mathbf{1a}^{\bullet+}$, $\mathrm{TCNB}^{\bullet-}$] undergoes fast ring opening followed by back electron transfer before the ionic dissociation.

Judging by the k_{add} value and assuming a similar rate constant for *E*-**4b**, the addition of 0.02 M of MA is sufficient to trap *E*-**4a** and *E*-**4b** completely. Indeed, the stereochemistry of **6a** and **6b** indicates that MA undergoes *endo* addition exclusively with the resulting *E*-**4a** and *E*-**4b**. While no formation of the MA adduct with *Z*-**4a** or *Z*-**4b** was observed in the trapping experiments, it is evident that the tautomerization of *Z*-**4a** and *Z*-**4b** to the corresponding benzophenones is too fast to be intercepted by MA. If the k_{add} value of *Z*-**4a** is assumed to be in the order of 10^6 M^{-1} s^{-1}, an impractically high concentration of MA is required to trap *Z*-**4a** in competition with its tautomerization with k = 1.2 × 10^7 s^{-1}. Additional work is in progress for further understanding of the electrocycloreversion of benzocyclobutenols by PET.

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8 **3a**: mp 145—147 °C. *m/Z* (70 eV), 347 (M$^+$, 21), 272 (30), 195 (52), 183 (13), 165 (45), 105 (58), 77 (100%).. ν_{max} (KBr) 2220 (CN), 1660 (CO) cm^{-1}. δ_H (200 MHz, CDCl$_3$) 4.42 (s, 2H), 7.3—7.4 (m, 2H), 7.4—7.5 (m, 3H), 7.5—7.6 (m, 2H), 7.6 (s, 1H), 7.7—7.75 (m, 2H), 7.99 (s, 1H). δ_C (50 MHz, CDCl$_3$) 38.03, 113.81 (CN), 114.31 (CN), 114.37 (CN), 114.80, 117.55, 119.24, 127.75, 128.80, 130.45, 130.87, 131.97, 132.16, 133.88, 135.40, 135.40, 136.74, 137.18, 138.17, 151.44, 197.59 (CO). **3b**: mp 153—156 °C. *m/Z* (70 eV), 375 (M$^+$, 89), 360 (68), 358 (40), 332 (18), 254 (26), 105 (100%). ν_{max} (KBr) 2220 (CN), 1665 (CO) cm^{-1}. δ_H (200 MHz, CDCl$_3$) 2.10 (s, 3H), 2.39 (s, 3H), 4.07 (s, 2H), 6.92 (s, 1H), 7.09 (s, 1H), 7.44 (AA'BB'C, J = 1.4, 7.2, 7.8 Hz, 2H,m-Ph), 7.59 (s, 1H), 7.6(m, 1H, p-Ph), 7.69 (AA'BB'C, J = 1.4, 6.8 Hz, 2H, o-Ph), 7.89 (s, 1H). δ_C (50 MHz, CDCl$_3$) 19.84, 21.27, 37.35, 113.72 (CN), 114.25 (CN), 114.48 (CN), 114.65, 117.44, 119.24, 129.11, 129.20, 129.57, 131.18, 132.63, 134.44, 135.89, 135.93, 136.59, 136.96, 137.20, 140.22, 150.64, 199.79 (CO).

9 Calculations by using Weller's equation suggest that free energy changes for electron-transfer quenching of the singlet excited TeCA by **1** are exothermic by −0.41, −0.70, and −0.65 eV for **1a**, **1b**, and **1c**, respectively. Their oxidation potentials are +2.09, +1.80, and +1.85 V (*vs.* SCE), respectively.

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12 Substantially the same transient behavior was observed in the laser flash photolysis of 2-methylbenzophenone in dichloromethane. The decay rate of 1.2×10^7 s^{-1} was also obtained for the initial fast decay due to *Z*-**4a**.

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