Generation of an *o*-Xylylene: Electrocyclization of 1,2-Bis(1-phenylvinyl)benzene promoted by Photoinduced Electron Transfer

Yasutake Takahashi, Yukako Ohya, Hiroshi Ikeda and Tsutomu Miyashi*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980-77, Japan

1,2-Bis(1-phenylvinyl)benzene undergoes electron-transfer induced electrocyclization to generate an *o*-xylylene derivative which can be trapped or observed spectroscopically.

Although electrocyclic reactions of hydrocarbon cation radicals have attracted considerable attention,[1–6] they are still much less well known than those of the corresponding neutral molecules. The utilization of radiolysis,[1,3] mass spectroscopic techniques[4] and photoinduced electron transfer[5,6] to probe such reactions has provided some examples of cycloreversions of cyclobutenes[3,4,6] and cyclohexa-1,3-diene.[1] However, relatively little has been learned about the reverse process, electrocyclization of butadieness, hexa-1,3,5-trienes and related compounds. We have found that the electrocyclization of 1,2-bis(1-phenylvinyl)benzene **1** to *o*-xylylene **2** can be promoted by electron transfer (ET).

Compound **1** is a good electron donor and forms electron donor–acceptor (EDA) complexes with tetracyanoethylene (TCNE), whose charge-transfer (CT) absorption maximum is 510 nm in methylene chloride. Upon photoirradiation of the CT band (λ > 400 nm) the original reddish–purple colour was gradually depleted and a TCNE adduct **3** was obtained in 50% isolated yield.[†] No reaction was observed either in the dark or upon irradiation without TCNE.

Comparable results were obtained in the ET photosensitized reaction of **1** with 9,10-dicyanoanthracene (DCA) as an acceptor sensitizer. The oxidation potential of **1**, +1.47 V *vs.* SCE, is low enough for exothermic ET from **1** to ^{1}DCA* in acetonitrile. Calculations using Weller's equation[7] show that the free energy change for ET from **1** to ^{1}DCA* is exothermic by −0.55 eV. In accord with this, DCA fluorescence can be quenched by **1** with rate constants of 1.24×10^{10} and 5.3×10^9 dm^3 mol^{-1} s^{-1} in acetonitrile and methylene chloride, respectively. When a solution of **1**, DCA and fumaronitrile (FN) in acetonitrile or methylene chloride was irradiated (λ > 360 nm) for 2 h, a FN adduct **4** was obtained in 90–95% yield.[†] No reaction proceeded in the dark or without DCA. Similar irradiation in oxygen-saturated solvents without FN resulted in the formation of endoperoxide **5**. The isolated yields were 27, 24 and 49% in acetonitrile, methylene chloride and benzene, respectively. Photooxygenation of **1** with methylene blue, a typical sensitizer for singlet oxygen ($^1O_2$), did not afford **5** but ended up with the recovery of **1**.

Evidence for the generation of **2** was provided by analogous sensitized photoreactions of **1** without a dienophile. Thus, irradiation of **1** and DCA in nitrogen-saturated methylene chloride produced a red colouration, which is due to the appearance of a new absorption band at λ_{max} = 446 nm. This absorption can be assigned to the formation of **2** since the addition of TCNE or FN to the red solution resulted in decolouration with the formation of **3** or **4**. Also in support of this assignment is that a diphenyl derivative of *o*-xylylene **6**, whose structure is very similar to that of **2**, is reported to have λ_{max} = 450 nm in methylcyclohexane.[8] Furthermore, photolysis (350 nm, RUL-3500) of a nitrogen-saturated [$^2H_3$]acetonitrile solution of **1** (0.5 cm^3; 0.025 mmol) and 1,4-dicyanonaphthalene in an NMR tube allowed us to observe **2** by ^{1}H NMR spectroscopy. On irradiation, new resonance signals appeared at δ 6.64 (2 H), 6.00 (2 H) and 2.66 (4 H). The former two signals are attributable to the alkenic protons of **2** and the latter to the methylene protons. After irradiation for 6 h a 60% yield of **2** was achieved.

Both photoexcitation of EDA complexes and photosensitization with cyanoaromatics are straightforward methods for ET. It is clear that photoinduced ET from **1** to the acceptors (Acc) is an important initial step. Cation radical $\mathbf{1}^{\cdot+}$ in a photogenerated ion radical pair [$\mathbf{1}^{\cdot+}$, Acc$^{\cdot-}$] may undergo electrocyclization to give $\mathbf{2}^{\cdot+}$. *o*-Xylylene **2** can be produced by back ET, possibly within the resulting ion pair [$\mathbf{2}^{\cdot+}$, Acc$^{\cdot-}$]. The [4 + 2] cycloaddition of **2** with dienophiles leads to adducts such as **3** and **4**. While formation of **5** by direct reaction of **1** with $^1O_2$ is shown to be unlikely, $^1O_2$ may react with **2** to give **5**. It is known that $^1O_2$ can be generated through the quenching of ^{1}DCA* by molecular oxygen.[9] At this stage, however, involvement of ground state molecular oxygen in the formation of **5** remains as an alternative possibility.

It is remarkable that electrocyclization of **1** to **2** can be promoted by photoinduced ET despite the loss of aromaticity of **1**. Although the detailed mechanism has yet to be investigated, the present reaction provides unique methodology for generation of *o*-xylylene derivatives. Additional experiments are under way to expand the understanding of electrocyclic reactions induced by ET.

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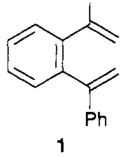

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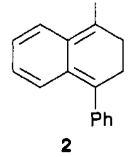

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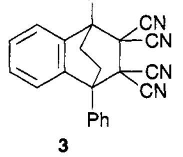

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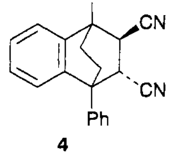

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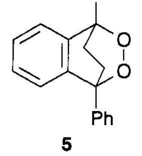

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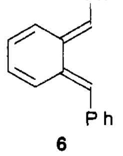

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Footnote

[†] A 10 cm^3 solution of **1** and TCNE (0.500 mmol each) was irradiated. For sensitized photolysis, a 10 cm^3 solution of **1** (0.500 mmol), FN (1.00 mmol), and DCA (0.005 mmol) was irradiated. Satisfactory elementary analyses were obtained for all new compounds and the structure was determined on the basis of their spectral data. *Selected data* for **3**: mp 282–283 °C; ν_{max}/cm^{-1} (KBr) 2240; δ_H (200 MHz, CDCl$_3$) 2.30 (2 H, m), 2.99 (2 H, m), 7.39 (4 H, m), 7.64 (6 H, m), 7.90 (4 H, m); δ_C (50 MHz, CDCl$_3$) 28.64, 51.39, 51.52, 111.27, 111.89, 127.36, 129.05, 129.14, 129.39, 129.66, 133.76, 136.48; *m*/*z* (70 eV) 410 (M$^+$, 0.2%), 283 (24), 282 (100), 191 (50). For **4**: mp 282.5–283 °C; ν_{max}/cm^{-1} (KBr) 2230; δ_H (200 MHz, CDCl$_3$) 2.24 (3 H, m), 2.74 (1 H, m), 3.56 (1 H, ddd, *J* = 0.6, 1.8, 4.0 Hz), 3.87 (1 H, d, *J* = 4.0 Hz), 6.70 (1 H, m), 7.25 (3 H, m), 7.52 (10 H, m); δ_C (50 MHz, CDCl$_3$) 27.88, 33.72, 40.04, 40.15, 45.72, 46.49, 118.82, 119.39, 125.03, 125.91, 127.69, 127.82, 127.95, 128.34, 128.85, 138.26, 138.62, 138.77, 142.03; *m*/*z* (25 eV) 360 (M$^+$, 16%), 283 (22), 282 (100), 281 (24), 191 (68). For **5**: mp 184–186 °C; δ_H (200 MHz, CDCl$_3$) 2.39 (2 H, m), 2.83 (2 H, m), 6.72 (2 H, m), 7.24 (2 H, m), 7.51 (10 H, m); δ_C (50 MHz, CDCl$_3$) 28.43, 80.82,

122.98, 127.15, 127.83, 128.46, 128.65, 137.20, 140.89. *m/z* (25 eV) 314 (M^+, 2%), 282 (73), 280 (100), 270 (42), 191 (51).

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