# Supporting Information

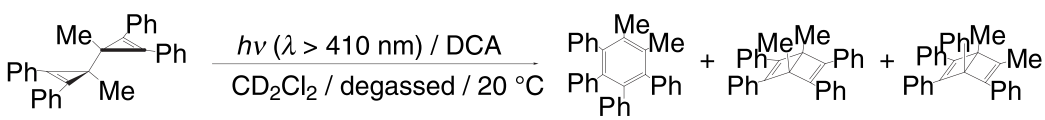
## Photoinduced Electron-transfer Bicyclopropenyl–benzene Rearrangements of 2,2',3,3'-Tetraphenylbicyclopropenyls: A New Mechanism via Dewar Benzene

Hiroshi Ikeda,* Yosuke Hoshi, Yuka Kikuchi, Futoshi Tanaka, and Tsutomu Miyashi

*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

**(1) Analyses of time-dependent change in the product ratios:** A $CD_2Cl_2$ (0.6 mL) solution containing **3** (0.06 mmol, 0.1 M) and DCA (0.01 mmol, 0.02 M[31]) in a Pyrex NMR tube was degassed by five repeated freeze (–196 °C)–pump ($10^{-2}$ Torr)–thaw (0 °C) cycles and then sealed at $10^{-2}$ Torr. The solution was irradiated through a cutoff filter ($\lambda$ > 410 nm for DCA) with a 2 kW Xe lamp at 20 ± 1 °C. The product ratios during photoreaction were determined by 200 MHz $^1$H NMR analyses (errors are ca. ± 2 %). The material balance was determined also by $^1$H NMR analyses using 1,1,2,2- or 1,1,1,2-tetrachloroethane as an internal standard for integration.

**(2) Time-dependent changes in the product ratios in the DCA-sensitized PET reaction of 3a.**




**3a** **4a** **6a** **7a**

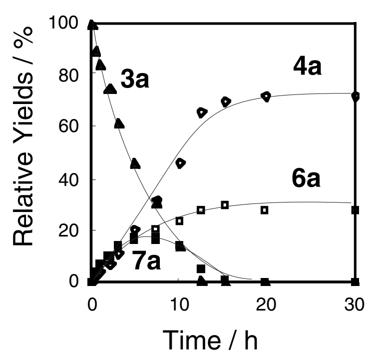



**Figure S1.** Time-dependent changes in the product ratios in the DCA-sensitized PET reaction of **3a**. A 0.6 mL solution was irradiated with a 2 kW Xe lamp through a cutoff filter. [**3a**] = 0.1 M. M. B. = 95%

**(3) Isolation of 6 and 7:** A photolysate obtained by similar PET reaction of **3** (0.2 mmol) and DCA (0.04 mmol) in $CH_2Cl_2$ (20 mL) for 80 min was separated by HPLC ($Al_2O_3$, *n*-hexane) after removal of solvent at room temperature in the dark. Structures of **6** and **7** were confirmed by chemical reactions (thermolyses) and spectroscopy, especially by $^1$H and $^{13}$C

NMR analyses. The physical data shown below were identical with those of **6** and **7** obtained independently by $Ag^+$-catalysed reactions.

**6a**: Colorless columns ($CH_2Cl_2$–*n*-hexane); mp 162–163 ˚C; MS (EI, 70 eV) *m/z* (relative intensity) 410 (100, $M^+$), 395 (8, $M^+$ – Me), 317 (12); IR (KBr) $\nu$ 2949, 1597, 1494, 1441, 775, 761, 743, 725, 692 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 1.70 (s, 6 H), 7.21–7.31 (m, 12 H), 7.38–7.43 (m, 8 H); $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 12.9 (2 C), 55.9 (2 C), 127.1 (8 C), 127.5 (4 C), 128.4 (8 C), 135.9 (4 C), 147.5 (4 C); Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.44; H, 6.30.

**7a** (thermally labile, purity 90%): Colorless oil; MS (EI, 70 eV) *m/z* (relative intensity) 410 (100, $M^+$) 395 (3, $M^+$ – Me), 317 (5); $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 1.03 (s, 3 H), 2.27 (s, 3 H), 7.18–7.32 (m, 12 H), 7.36 (m, 2 H), 7.40 (m, 2 H), 7.56 (m, 4 H); $^{13}C$ NMR (150 MHz, $CDCl_3$) $\delta$ 11.2, 14.3, 59.1, 63.2, 126.0, 126.5, 127.0 (2 C), 127.1 (2 C), 127.48, 127.52 (2 C), 127.7, 128.1 (2 C), 128.2 (2 C), 128.3 (2 C), 128.5 (2 C), 128.6 (2 C), 135.2, 135.3, 135.8, 139.1, 142.5, 143.6, 148.5, 150.0.

**6b**[3b]: Colorless cubes ($CH_2Cl_2$–*n*-hexane); mp 145–146 ˚C; MS (EI, 70 eV) *m/z* (relative intensity) 396 (100, $M^+$) 381 (6, $M^+$ – Me), 303 (7); IR (KBr) $\nu$ 2951, 1195, 1441, 1325, 772, 748, 725, 692 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$ 1.78 (s, 3 H), 4.08 (s, 1 H), 7.20–7.33 (m, 12 H), 7.41–7.53 (m, 8 H) [lit.[3b] $\tau$ 8.22 (s, 3H), 5.93 (s, 1 H)]; $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 15.8, 50.6, 52.9, 126.6 (4 C), 127.1 (4 C), 127.5 (2 C), 127.6 (2 C), 128.4 (4 C), 128.5 (4 C), 136.0 (2 C), 136.1 (2 C), 143.9 (2 C), 148.7 (2 C); Anal. Calcd for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 93.60; H, 6.29.

**7b** (thermally labile, purity 94%): Colorless oil; MS (EI, 70 eV) *m/z* (relative intensity) 396 (100, $M^+$), 381 (5, $M^+$ – Me), 303 (5); $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 2.29 (s, 3 H), 3.72 (s, 1 H), 7.15–7.28 (m, 10 H), 7.33–7.39 (m, 6 H), 7.53–7.62 (m, 4 H); $^{13}C$ NMR (150 MHz, $CDCl_3$) $\delta$ 16.6, 57.0, 58.6, 126.0, 126.2 (2 C), 126.7, 126.9 (2 C), 127.3 (2 C), 127.5 (2 C), 127.6, 128.0, 128.3 (2 C), 128.35 (2 C), 128.38 (2 C), 128.5 (2 C), 135.4, 135.6, 136.2, 140.9, 144.3, 145.25, 145.31, 146.0.

**(4) Determination of $\Phi_c$:** (1) Determination of usual quantum efficiency ($\Phi$): A $CH_2Cl_2$ solution (3 mL) containing **3** (0.03 mmol, 10 mM) and DCA (0.47 mM) was irradiated with light of wavelength at $\lambda_{max}$ = 437 ± 12 nm under $N_2$ at 20 ± 1 °C. Light of this wavelength was obtained from a 500 W Hg-Xe lamp through aqueous $CuSO_4$ solution filter, a Toshiba cutoff filter UV-37, and an interference filter ($\lambda_{max}$ =437 nm). Aberchrome 540P was used as an actinometer. The conversion was 10 ± 5% in all cases. After irradiation and removal of solvent at room temperature in the dark, the photolysate was analyzed by $^1H$ NMR. The values of $\Phi$ were obtained as the mean values of three separate runs. (2) Conversion of $\Phi$ to $\Phi_{cor}$: The $\Phi$ values were converted to $\Phi_{cor}$ using the Stern–Volmer constants in $CH_2Cl_2$ ($k_q\tau$ = 217 and 214 $M^{-1}$ for **3a** and **3b**, respectively) and the following equations: $\Phi_{cor} = \Phi \times (1 + k_q\tau[\mathbf{3}]) / k_q\tau[\mathbf{3}]$ , where [**3**] = 10 mM.

**(5) The Cartesian coordinates and the $\Sigma\rho$ and $\Sigma q$ values for 3a$^{\bullet+}$ and 3b$^{\bullet+}$ (ROB3LYP/6-31G(p)).**

Table S1. The Cartesian Coordinates, the Sum of the Partial Spin and Charge Densities ($\Sigma\rho$ and $\Sigma q$) of **3a**$^{\bullet+}$ Obtained by ROB3LYP/6-31G(p) Calculations (PC GAMESS ver. 6.3)

| | | Cartesian Coordinates | | | | |
|---|---|---|---|---|---|---|
| No | Atom | x | y | z | $\Sigma\rho$ | $\Sigma q$ |
| 1 | C | –0.578180059 | –0.601643192 | 0.000000000 | +0.068315 | –0.125195 |
| 2 | C | 0.578180059 | 0.601643192 | 0.000000000 | +0.068315 | –0.125195 |
| 3 | C | 0.044441275 | –1.994028396 | 0.000000000 | +0.029135 | –0.223340 |
| 4 | C | –0.044441275 | 1.994028396 | 0.000000000 | +0.029135 | –0.223340 |
| 5 | C | –1.851076405 | –0.286314400 | 0.668823831 | +0.135174 | –0.010606 |
| 6 | C | 1.851076405 | 0.286314400 | –0.668823831 | +0.135174 | –0.010606 |
| 7 | C | –1.851076405 | –0.286314400 | –0.668823831 | +0.135174 | –0.010606 |
| 8 | C | 1.851076405 | 0.286314400 | 0.668823831 | +0.135174 | –0.010606 |
| 9 | C | –2.529757465 | –0.205526834 | 1.926000500 | +0.009422 | –0.036729 |
| 10 | C | 2.529757465 | 0.205526834 | –1.926000500 | +0.009422 | –0.036729 |
| 11 | C | –2.529757465 | –0.205526834 | –1.926000500 | +0.009422 | –0.036729 |
| 12 | C | 2.529757465 | 0.205526834 | 1.926000500 | +0.009422 | –0.036729 |
| 13 | C | –1.877916894 | –0.637881917 | 3.089019655 | +0.017847 | –0.089822 |
| 14 | C | 1.877916894 | 0.637881917 | –3.089019655 | +0.017847 | –0.089822 |
| 15 | C | –1.877916894 | –0.637881917 | –3.089019655 | +0.017847 | –0.089822 |
| 16 | C | 1.877916894 | 0.637881917 | 3.089019655 | +0.017847 | –0.089822 |
| 17 | C | –3.838586836 | 0.286260837 | 2.022389493 | +0.016955 | –0.043581 |
| 18 | C | 3.838586836 | –0.286260837 | –2.022389493 | +0.016955 | –0.043581 |
| 19 | C | –3.838586836 | 0.286260837 | –2.022389493 | +0.016955 | –0.043581 |
| 20 | C | 3.838586836 | –0.286260837 | 2.022389493 | +0.016955 | –0.043581 |
| 21 | C | –2.519770591 | –0.583964845 | 4.313838055 | +0.001074 | –0.142107 |
| 22 | C | 2.519770591 | 0.583964845 | –4.313838055 | +0.001074 | –0.142107 |
| 23 | C | –2.519770591 | –0.583964845 | –4.313838055 | +0.001074 | –0.142107 |
| 24 | C | 2.519770591 | 0.583964845 | 4.313838055 | +0.001074 | –0.142107 |
| 25 | C | –4.475730728 | 0.342695143 | 3.248605042 | +0.000622 | –0.148279 |
| 26 | C | 4.475730728 | –0.342695143 | –3.248605042 | +0.000622 | –0.148279 |
| 27 | C | –4.475730728 | 0.342695143 | –3.248605042 | +0.000622 | –0.148279 |
| 28 | C | 4.475730728 | –0.342695143 | 3.248605042 | +0.000622 | –0.148279 |
| 29 | C | –3.818347171 | –0.092973667 | 4.395183862 | +0.018616 | –0.093168 |
| 30 | C | 3.818347171 | 0.092973667 | –4.395183862 | +0.018616 | –0.093168 |
| 31 | C | –3.818347171 | –0.092973667 | –4.395183862 | +0.018616 | –0.093168 |
| 32 | C | 3.818347171 | 0.092973667 | 4.395183862 | +0.018616 | –0.093168 |
| 33 | H | –0.880182835 | –1.020312598 | 3.024472390 | +0.000105 | +0.159776 |
| 34 | H | 0.880182835 | 1.020312598 | –3.024472390 | +0.000105 | +0.159776 |
| 35 | H | –0.880182835 | –1.020312598 | –3.024472390 | +0.000105 | +0.159776 |
| 36 | H | 0.880182835 | 1.020312598 | 3.024472390 | +0.000105 | +0.159776 |
| 37 | H | –4.347186402 | 0.624590313 | 1.144789643 | +0.000050 | +0.148634 |
| 38 | H | 4.347186402 | –0.624590313 | –1.144789643 | +0.000050 | +0.148634 |
| 39 | H | –4.347186402 | 0.624590313 | –1.144789643 | +0.000050 | +0.148634 |
| 40 | H | 4.347186402 | –0.624590313 | 1.144789643 | +0.000050 | +0.148634 |
| 41 | H | –2.018537999 | –0.923426701 | 5.196207373 | +0.000006 | +0.162835 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 42 | H | 2.018537999 | 0.923426701 | –5.196207373 | +0.000006 | +0.162835 |
| 43 | H | –2.018537999 | –0.923426701 | –5.196207373 | +0.000006 | +0.162835 |
| 44 | H | 2.018537999 | 0.923426701 | 5.196207373 | +0.000006 | +0.162835 |
| 45 | H | –5.474305422 | 0.721226624 | 3.314886802 | +0.000004 | +0.167182 |
| 46 | H | 5.474305422 | –0.721226624 | –3.314886802 | +0.000004 | +0.167182 |
| 47 | H | –5.474305422 | 0.721226624 | –3.314886802 | +0.000004 | +0.167182 |
| 48 | H | 5.474305422 | –0.721226624 | 3.314886802 | +0.000004 | +0.167182 |
| 49 | H | –4.314554957 | –0.050373326 | 5.342732918 | +0.000056 | +0.170215 |
| 50 | H | 4.314554957 | 0.050373326 | –5.342732918 | +0.000056 | +0.170215 |
| 51 | H | –4.314554957 | –0.050373326 | –5.342732918 | +0.000056 | +0.170215 |
| 52 | H | 4.314554957 | 0.050373326 | 5.342732918 | +0.000056 | +0.170215 |
| 53 | H | –0.733265691 | –2.744282904 | 0.000000000 | +0.001428 | +0.122223 |
| 54 | H | 0.733265691 | 2.744282904 | 0.000000000 | +0.001428 | +0.122223 |
| 55 | H | 0.661249424 | –2.141554505 | –0.875790767 | +0.000630 | +0.118807 |
| 56 | H | –0.661249424 | 2.141554505 | 0.875790767 | +0.000630 | +0.118807 |
| 57 | H | 0.661249424 | –2.141554505 | 0.875790767 | +0.000630 | +0.118807 |
| 58 | H | –0.661249424 | 2.141554505 | –0.875790767 | +0.000630 | +0.118807 |

Heat of Formation: –1226.2109053997 a.u.

Table S2. The Cartesian Coordinates, the Sum of the Partial Spin and Charge Densities ($\Sigma\rho$ and $\Sigma q$) of **3b**$^{\bullet+}$ Obtained by ROB3LYP/6-31G(p) Calculations (PC GAMESS ver. 6.3)

| | | Cartesian Coordinates | | | | |
|---|---|---|---|---|---|---|
| No | Atom | x | y | z | $\Sigma\rho$ | $\Sigma q$ |
| 1 | C | –0.559549225 | –0.639476666 | 0.000000000 | +0.033709 | –0.129180 |
| 2 | C | 0.539463289 | 0.446694960 | 0.000000000 | +0.008038 | –0.127390 |
| 3 | C | –0.037659591 | –2.070746738 | 0.000000000 | +0.005954 | –0.231190 |
| 4 | H | 0.122636513 | 1.441623378 | 0.000000000 | +0.034269 | +0.187870 |
| 5 | C | –1.872751714 | –0.274072149 | –0.650569266 | +0.009224 | –0.050900 |
| 6 | C | –1.872751714 | –0.274072149 | 0.650569266 | +0.009224 | –0.050900 |
| 7 | C | 1.854499770 | 0.271795248 | –0.684860900 | +0.278684 | +0.005144 |
| 8 | C | 1.854499770 | 0.271795248 | 0.684860900 | +0.278684 | +0.005144 |
| 9 | C | –2.533864619 | –0.145178871 | –1.930244985 | +0.000220 | –0.010730 |
| 10 | C | –2.533864619 | –0.145178871 | 1.930244985 | +0.000220 | –0.010730 |
| 11 | C | –1.960843095 | –0.712484975 | –3.071453528 | +0.001083 | –0.122360 |
| 12 | C | –1.960843095 | –0.712484975 | 3.071453528 | +0.001083 | –0.122360 |
| 13 | C | –3.752086937 | 0.528302358 | –2.051367655 | +0.001096 | –0.066330 |
| 14 | C | –3.752086937 | 0.528302358 | 2.051367655 | +0.001096 | –0.066330 |
| 15 | C | –2.591354160 | –0.611884936 | –4.302496420 | +0.000087 | –0.134420 |
| 16 | C | –2.591354160 | –0.611884936 | 4.302496420 | +0.000087 | –0.134420 |
| 17 | C | –4.379054458 | 0.630972572 | –3.282854930 | +0.000005 | –0.139530 |
| 18 | C | –4.379054458 | 0.630972572 | 3.282854930 | +0.000005 | –0.139530 |
| 19 | C | –3.800907947 | 0.062154979 | –4.411549968 | +0.001098 | –0.112480 |
| 20 | C | –3.800907947 | 0.062154979 | 4.411549968 | +0.001098 | –0.112480 |
| 21 | H | –1.038028888 | –1.250150360 | –2.987926818 | +0.000053 | +0.138567 |
| 22 | H | –1.038028888 | –1.250150360 | 2.987926818 | +0.000053 | +0.138567 |
| 23 | H | –4.202845862 | 0.972367629 | –1.188791387 | +0.000003 | +0.142513 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 24 | H | –4.202845862 | 0.972367629 | 1.188791387 | +0.000003 | +0.142513 |
| 25 | H | –2.149116942 | –1.062601892 | –5.167337796 | +0.000001 | +0.148075 |
| 26 | H | –2.149116942 | –1.062601892 | 5.167337796 | +0.000001 | +0.148075 |
| 27 | H | –5.312301996 | 1.149320965 | –3.362547443 | +0.000001 | +0.156814 |
| 28 | H | –5.312301996 | 1.149320965 | 3.362547443 | +0.000001 | +0.156814 |
| 29 | H | –4.288867868 | 0.140306404 | –5.361160506 | +0.000004 | +0.157322 |
| 30 | H | –4.288867868 | 0.140306404 | 5.361160506 | +0.000004 | +0.157322 |
| 31 | C | 2.531374614 | 0.244704126 | –1.918894368 | +0.037995 | –0.073080 |
| 32 | C | 2.531374614 | 0.244704126 | 1.918894368 | +0.037995 | –0.073080 |
| 33 | C | 1.802239766 | 0.494530178 | –3.098927745 | +0.041003 | –0.051150 |
| 34 | C | 1.802239766 | 0.494530178 | 3.098927745 | +0.041003 | –0.051150 |
| 35 | C | 3.916275719 | –0.004081815 | –2.006339423 | +0.038882 | –0.008750 |
| 36 | C | 3.916275719 | –0.004081815 | 2.006339423 | +0.038882 | –0.008750 |
| 37 | C | 2.439680534 | 0.500370755 | –4.323148636 | +0.002691 | –0.153360 |
| 38 | C | 2.439680534 | 0.500370755 | 4.323148636 | +0.002691 | –0.153360 |
| 39 | C | 4.545814940 | –0.002410422 | –3.232138393 | +0.002716 | –0.160600 |
| 40 | C | 4.545814940 | –0.002410422 | 3.232138393 | +0.002716 | –0.160600 |
| 41 | C | 3.808458139 | 0.251319501 | –4.389449886 | +0.043901 | –0.066660 |
| 42 | C | 3.808458139 | 0.251319501 | 4.389449886 | +0.043901 | –0.066660 |
| 43 | H | 0.751080078 | 0.684806670 | –3.035886378 | +0.000107 | +0.190026 |
| 44 | H | 0.751080078 | 0.684806670 | 3.035886378 | +0.000107 | +0.190026 |
| 45 | H | 4.479483728 | –0.199941409 | –1.119275878 | +0.000125 | +0.157416 |
| 46 | H | 4.479483728 | –0.199941409 | 1.119275878 | +0.000125 | +0.157416 |
| 47 | H | 1.886183341 | 0.697425636 | –5.216666151 | +0.000015 | +0.180429 |
| 48 | H | 1.886183341 | 0.697425636 | 5.216666151 | +0.000015 | +0.180429 |
| 49 | H | 5.595861982 | –0.193713724 | –3.298296489 | +0.000016 | +0.179532 |
| 50 | H | 5.595861982 | –0.193713724 | 3.298296489 | +0.000016 | +0.179532 |
| 51 | H | 4.301854119 | 0.254190861 | –5.339544296 | +0.000126 | +0.185435 |
| 52 | H | 4.301854119 | 0.254190861 | 5.339544296 | +0.000126 | +0.185435 |
| 53 | H | –0.865475117 | –2.764577603 | 0.000000000 | +0.000071 | +0.129056 |
| 54 | H | 0.568471651 | –2.278083967 | –0.875287955 | –0.00016 | +0.094489 |
| 55 | H | 0.568471651 | –2.278083967 | 0.875287955 | –0.00016 | +0.094489 |

Heat of Formation: –1187.1892213029 a.u.

**Note and Reference**

(31) The sample solution was slightly suspended with DCA. The actual concentrations of DCA are the saturated ones, which are *ca.* $2 \times 10^{-3}$ M at 20 °C.[32]

(32) Ikeda, H.; Aburakawa, N.; Tanaka, F.; Fukushima, T.; Miyashi, T. *Eur. J. Org. Chem.* **2001**, 3445–3452.

(End)