Supporting Information
for
Electron-promoted Cope Cyclization Studies of 2,5-Diphenyl substituted-1,5-Hexadiene Radical Anions

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This supplemental material consists of the following sections:

Experimental Section

General Methods

^{1}H Spectra (300MHz) and ^{13}C Spectra (300MHz) were recorded using $CDCl_3$ as a solvent.

(I) Fragmentation pattern for 2,5-Diaryl-1,5-hexadienes.

The radical anions of 2,5-diphenyl substituted 1,5-hexadienes (2b-2i) were generated using thermal electrons in the Flowing Afterglow Triple Quadrupole Mass Spectrometer. The relative yields for the ion fragments and their neutral losses are shown below.

2b: m/z 270 (0.33) and m/z 163 (1.0)

$$\underset{\text{m/z 270}}{C_{18}H_{16}F_2^{\bullet -}} \xrightarrow[\text{(m/z 107)}]{-C_7H_4F} \underset{\text{m/z 163}}{C_{11}H_{12}F^{-}}$$

2c: m/z 270 (0.15), m/z 148 (1.0) m/z 60 (0.42).

$$\underset{\text{m/z 270}}{C_{18}H_{16}F_2^{\bullet -}} \xrightarrow[\text{(m/z 122)}]{-C_8H_7F} \underset{\text{m/z 148}}{C_{10}H_9F^{\bullet -}} \xrightarrow[\text{(m/z 88)}]{-C_7H_4} \underset{\text{m/z 60}}{C_3H_5F^{-}}$$

2d: m/z 324 (0.09), m/z 308 (0.65), m/z 276 (0.71), m/z 233 (0.25), m/z 217(1.0), m/z 199 (0.38), m/z 179 (0.31), m/z 163 (0.69).

$$\underset{}{C_{18}H_{16}N_2O_4^{\bullet -}} \xrightarrow[\text{(m/z 16)}]{-O} \underset{\text{m/z 308}}{C_{18}H_{16}N_2O_3^{\bullet -}} \xrightarrow[\text{(m/z 32)}]{-O_2} \underset{\text{m/z 276}}{C_{18}H_{16}N_2O_2^{\bullet -}}$$

$$C_{18}H_{16}N_2O_4^{\bullet -} \xrightarrow[\text{(m/z 91)}]{-C_7H_7} \underset{\text{m/z 233}}{C_{11}H_9N_2O_4^{\bullet -}}$$

$$\underset{\text{m/z 233}}{C_{11}H_9N_2O_4^{\bullet -}} \xrightarrow[\text{(m/z 16)}]{-O} \underset{\text{m/z 217}}{C_{11}H_9N_2O_3^{\bullet -}} \xrightarrow[\text{(m/z 18)}]{-H_2O} \underset{\text{m/z 199}}{C_{11}H_7N_2O_2^{\bullet -}}$$

2e: m/z 302 (0.20), m/z 35 (1).

$$C_{18}H_{16}Cl_2^{\bullet -} \xrightarrow[\text{(m/z 232)}]{-C_{18}H_{16}} Cl^{-}$$

m/z 302 m/z 35

2f: m/z 318 (0.20) and m/z 148 (1.0).

$$C_{22}H_{22}O_2^{\bullet -} \xrightarrow[\text{(m/z 170)}]{-C_{12}H_{10}O} C_{10}H_{12}O^{-}$$

m/z 318 m/z 148

2g: m/z 302 (0.20), m/z 35 (1).

$$C_{18}H_{16}Cl_2^{\bullet -} \xrightarrow[\text{(m/z 232)}]{-C_{18}H_{16}} Cl^{-}$$

m/z 302 m/z 35

2h: m/z 370 (0.04), m/z 342 (1.0), m/z 202 (0.26), m/z 200 (0.07) and m/z 122 (0.03).

$$C_{20}H_{16}F_6^{\bullet -} \xrightarrow[\text{(m/z 28)}]{-C_2H_4} C_{18}H_{12}F_6^{-} \xrightarrow[\text{(m/z 141)}]{-C_7F_3} C_{11}H_{12}F_3^{-}$$

m/z 370 m/z 342 m/z 202

$$C_{11}H_{12}F_3^{-} \xrightarrow[\text{(m/z 2)}]{-H_2} C_{11}H_{10}F_3^{-}$$

$$C_{11}H_{10}F_3^{-} \xrightarrow[\text{(m/z 77)}]{-C_3H_3F_2} C_8H_7F^{-}$$

m/z 200 m/z 122

2i: m/z 370 (1.0), m/z 342 (0.16) and m/z 187 (0.04).

$$C_{20}H_{16}F_6^{\bullet -} \xrightarrow[\text{(m/z 28)}]{-C_2H_4} C_{18}H_{12}F_6^{-} \xrightarrow[\text{(m/z 155)}]{-C_8H_2F_3} C_{10}H_{10}F_3^{-}$$

m/z 370 m/z 342 m/z 60

(II) Synthesis of 2,5-Dicyano-1,5-hexadiene(1)

2,5-dicyano-1,5-hexadiene was prepared by refluxing 3 equivalents of CuCN in dry DMF for one hour under a nitrogen atmosphere.[1] The mixture was then cooled to room temperature, and 2,,5-dibromo-1,5-hexadiene[1] was added. The mixture was then heated overnight at 130 °C. After cooling down the reaction to room temperature, the reaction was stirred for one hour in 6M aq. NH_3, and then filtered. The precipitate was then washed with water three times. The combined water layers were washed with dichloromethane which was then combined with ether layers and dried over magnesium sulfate. The solvents were evaporated and the pure product was obtained by flash column chromatography using silica gel with 5% ethylacetate/hexane solvent.

(III) Synthesis of 2, 5-Diaryl-1,5-hexadienes (2b-2i)

The synthesis of 2,5-Diaryl-1,5-hexadienes is based on the $ZnCl_2$-based condensation reaction of the substituted methyl ketones and α-bromomethyl ketones followed by methynelation using the Nysted reaction to afford the hexadienes. Alternate substitution on the aromatic group was achieved by using a Li/halogen exchange to prepare 2f.

(2a) General Procedure for preparation of 1,4-Diketones[2]: To a flame-dried flask was added commercially available anhydrous $ZnCl_2$ (2.73g, 20mmol) which was dried by melting under vacuum (1 torr) at 250-300 °C for 10-15 min. The flask was then allowed to cool under vacuum, upon which dry benzene (15 ml), diethyl amine (15 mmol) and t-BuOH (15 mmol) were successively added. The above mixture was stirred at room temperature for approximately 3 h until the zinc chloride dissolved to form a clear

solution. Then methyl ketone(2.48g, 15 mmol) and the α-bromo ketone(2.44g, 10 mmol) were added to the reaction mixture. The mixture was stirred for 1h and allowed to stand for 3-7 days at r.t. It was observed that the bis-ketones having fluoro sustituents were difficult to crystallize and a needed longer reaction time. The reaction was subsequently quenched with 5% aq. H_2SO_4 and filtered. The crystalline products were washed successively with benzene, water and methanol and recystallized. The yields of the diketones varied from 45 % to 70%. The NMR data for all diketones agree with previously reported literature values.[2,3]

(2b) General Procedure for preparation of 2, 5-Diaryl-1,5-hexadienes: [4]

Nysted reagent (20% wt. suspension in THF), (2.89 g, 6.33 mmol) was transferred to a pre-weighed flask and 2 ml of THF was added so as to dilute the reagent. The flask was then cooled to 0°C and a solution of 1M $TiCl_4$ (5.1 ml, 5.07 mmol) in THF was added slowly. The resulting mixture was stirred at 0^oC for 5 min and 1,4-diketone (0.83g, 2,53 mmol) dissolved in THF was slowly transferred to the reaction mixture. The temperature of the bath was raised to 18° C and the reaction was monitored by thin layer chromatography and quenched (using 1M HCl) within 3-4 hours of the starting reaction time even though a small amount of the starting material remained. If the reaction is left to run for longer times, it resulted in unwanted side products. The reaction mixture was extracted with hexanes (3x30 ml). The combined organic layer was washed with brine, dried over Na_2SO_4 and the solvent was evaporated to get the crude product. The crude mixture was purified by flash column chromatography (100 % hexanes to 3 %

ethylacetate-97 % hexanes) to get yields varying from 50 %-65 %. The FTIR, ^{1}H and ^{13}C NMR absorptions are listed below.

(2c) Synthesis of 4, 4'-diacetyl-2,5-diphenyl-1,5-hexadiene (2f)

To a solution of 4, 4'-dibromo-2,5-diphenyl-1,5-hexadiene (0.164g, 0.39 mmol) in THF (5 ml) at −78 °C was added n-butyllithium (0.34 ml, 0.86 mmol). After stirring for 30 minutes at −78 °C, acetic anhydride (0.0872 ml, 0.86 mmol) was added dropwise to the reaction mixture.[5] After stirring for 3 hours, the reaction was quenched with water and extracted with hexanes (3x10 ml), washed with saturated sodium chloride solution (5 ml) and the organic layer was dried over Na_2SO_4. The solvent was removed in vacuo to give the crude product which was purified by column chromatography (3% ethylacetate, 98% hexane) to give pure 2f (0.100 g, 60 %).

(III) Structural Characterization of 2, 5-Diaryl-1,5-hexadienes.

(2b) p-F: IR (film) $\nu_{max,}$: 3849, 3745, 3640, 3071, 3045, 2921, 2849, 2361, 1602, 1508, 1232, 1160, 1097, 1009, 898, 838, 817, 739 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (4H, t, J = 8.2 Hz), 7.10 (4H, t, J = 8.8 Hz), 5.31 (2H, s), 5.10 (2H, s), 2.69 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 164.0, 160.7, 146.9, 137.1, 127.9, 127.7, 115.3, 115.1, 112.7, 34.3.

(2c) m-F: IR (film) $\nu_{max,}$: 3928, 3775, 3333, 3084, 2927, 2366, 2239, 1729, 1609, 1581, 1485, 1426, 1302, 1266, 1213, 1156, 1117, 898, 873, 786, 722 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36 (2H, q, J = 5.9 Hz), 7.25 (2H, d, J = 7.0 Hz), 7.16 (2H, d, J = 10.5 Hz), 7.06 (2H, t, J = 10.6 Hz), 5.39 (2H, s), 5.15 (2H, s), 2.7 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 164.6, 161.3, 146.7, 143.5, 129.9, 129.8, 121.8, 114.4, 114.2, 113.9 113.3, 113.0, 34.1.

(2d) p-NO_2: IR (film) ν_{max}: 3854, 3745, 3689, 3675, 2928, 2360, 2342, 1700, 1507, 1343, 1109, 1081, 924, 853, 716, 765, 735 cm^{-1}. δ 8.19 (4H, d, J = 8.7 Hz), 7.50 (4H, d, J = 8.2 Hz), 5.41 (2H, s), 5.18 (2H, s), 2.65 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 171.3, 147.5, 145.8, 127.0, 123.8, 116.7, 33.9.

(2e) p-Cl: IR (film) ν_{max} : 3854, 3745, 3649, 2916, 2342, 2360, 1700, 1540, 1098, 1010, 903, 837, 765, 732 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37 (8H, m), 5.33 (2H, s), 5.11 (2H, s), 2.67 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 146.8, 139.5, 133.3, 128.5, 127.5, 113.4, 34.1.

(2f) p-$COCH_3$: IR (film) ν_{max} 3854, 3745, 3676, 2921, 2856, 2360, 2342, 1700, 1540, 1198, 1169, 1016, 915, 895, 849, 778, 719 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43 (6H, m), 7.14 (2H, d, J = 8.8 Hz), 5.36 (2H, d, J = 4.7 Hz), 5.13 (2H, s), 2.72 (6H, s), 2.39 (2H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 164.0, 160.7, 146.9, 137.1, 127.9, 115.3, 112.7, 34.3.

(2g) m-Cl: IR (film) ν_{max}: 3838, 3745, 3649, 3082, 2925, 2849, 2360, 1700, 1648, 1556, 1292, 1162, 1079, 884, 788, 721 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42 (2H, s), 7.33 (6H, m), 5.36 (2H, s), 5.14 (2H, s), 2.68 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 146.7, 143.0, 134.4, 129.6, 127.5, 126.4, 124.4, 114.1, 34.0.

(2h) m-CF_3: IR (film) ν_{max} : 3854, 3745, 3649, 2919, 2856, 2360, 2342, 1700, 1648, 1540, 1504, 1331, 1165, 1126, 1073, 900, 805, 719 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66-7.49 (8H, m), 5.40 (2H, s), 5.2 (2H, s), 2.73 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 146.6, 141.8, 129.5, 128.9, 124.3, 123.0, 114.6, 34.1, 29.8.

(2i) p-CF_3: IR (film) ν_{max} : 3854, 3745, 3689, 2360, 2342, 1700, 1540, 1337, 1168, 1120, 913, 850, 805 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (4H, d, J = 7.6 Hz), 7.47 (4H, d, J = 8.2 Hz), 5.35 (2H, s), 5.13 (2H, s), 2.66 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 146.7, 144.6, 126.5, 125.4, 125.3, 114.9 33.9.

(2j) p-Br: IR (film) ν_{max} : 3854, 3745, 3689, 2360, 2342, 1700, 1540, 1337, 1168, 1120, 913, 850, 805 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54 (4H, d, J = 8.2 Hz), δ 7.32 (4H, d, J = 8.2 Hz), δ 5.34 (2H, s), 5.11 (2H, s), 2.67 (4H, s). ^{13}C NMR ($CDCl_3$, 300 MHz): 147.8, 139.9, 131.5, 127.9, 121.5, 113.5, 34.0.

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