A New Reaction of Aryl Aldehydes with Aryl Acetylenes in the Presence of Boron Trihalides

George W. Kabalka,* Zhongzhi Wu, and Yuhong Ju

Departments of Chemistry and Radiology, The University of Tennessee, Knoxville, TN 37996-1600

Supporting Information

General Considerations: All glassware was dried in an oven at 120 ^{o}C and flushed with dry argon. All reactions were carried out under argon atmosphere. CH_2Cl_2 was distilled over CaH_2. All Aldehydes and Alkynes were purchased from Aldrich and used as received. Boron trichloride (1M hexane solution) was purchased from Aldrich. Boron tribromide (neat) was purchased from Aldrich and diluted to 1M CH_2Cl_2 solution. Prodcuts were purified by flash chromatography using silica gel (60 Å, 230-400 mesh) with hexanes as eluent except for **3e** and **4e** (Hexanes:EtOAc = 9:1 as eluent). Elemnetal Analyses were performed by Atlantic Microlabs Inc., Norcross, GA. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker 250 MHz instrument with chemical shifts reported relative to TMS. In cases where different isomers were isolated, the NMR shifts of all isomers are reported.

Representative procedure for the synthesis of 1,3,5-triaryl-1,5-dichloro-1,4-pentadienes (**3a-3j**). 4-Fluorobenzaldehyde (0.92 g, 7.4 mmol) and phenylacetylene (1.51 g, 14.8 mmol) were palced in a dry argon-flushed, 50 mL round-bottomed flask equipped with a stirring bar and dissolved in 20 mL dry CH_2Cl_2. Boron trichloride (8.0 mmol) 8.0 mL of a 1.0 M hexane solution) was added via a syringe. The solution was allowed to stir for 2hrs at 0 ^{o}C and then for 6 hrs at room temperature. The reaction

solution gradually truned dark purple. The resulting mixture was hydrolyzed with water and extracted with hexanes. The organic layer was seperated and dried over anhydrous $MgSO_4$. The product was isolated by flash column chromatography.

1,3,5-triphenyl-1,5-dichloro-1,4-pentadiene (**3a**). ^{1}H NMR: δ 7.57-7.21 (m, 15H), 6.26 (d, 1H, J = 9.2 Hz), 6.19 (d, 1H, J = 10.6 Hz), 4.88 (t, 1H, J = 10.1 Hz). ^{13}C NMR: δ 141.5, 137.6, 136.7, 133.7, 129.0, 128.9, 128.8, 128.3, 127.6, 127.2, 126.9, 126.5, 45.6. Anal. Calcd for $C_{23}H_{18}Cl_2$: C, 75.62; H, 4.97. Found: C, 75.48 ; H, 4.88.

1,5-dichloro-3-(4-fluorophenyl)-1,5-diphenyl-1,4-pentadiene (**3b**). ^{1}H NMR: δ 7.58-6.99 (m, 14H), 6.22 (d, 1H, J = 9.1 Hz), 6.15 (d, 1H, J = 10.4 Hz), 4.85 (t, 1H, J = 9.8 Hz). ^{13}C NMR: δ 163.7, 159.8, 137.4, 137.1, 136.6, 133.9, 133.3, 129.0, 128.9, 128.8, 128.7, 128.4, 127.3, 126.6, 115.8, 115.5, 44.9. Anal. Calcd for $C_{23}H_{17}Cl_2F$: C, 72.07 ; H, 4.47. Found: C, 72.32 ; H, 4.52.

1,5-dichloro-3-(4-bromophenyl)-1,5-diphenyl-1,4-pentadiene (**3c**). ^{1}H NMR: δ 7.56-7.09 (m, 14H), 6.21 (d, 1H, J = 9.1 Hz), 6.13 (d, 1H, J = 10.5 Hz), 4.81 (t, 1H, J = 9.9 Hz). ^{13}C NMR: δ 140.4, 137.3, 136.5, 134.1, 133.5, 131.9, 129.1, 129.0, 128.7, 128.4, 126.9, 126.5, 120.8, 45.0. Anal. Calcd for $C_{23}H_{17}BrCl_2$: C, 62.19 ; H, 3.86. Found: C, 62.35 ; H, 3.84.

1,5-dichloro-1,5-diphenyl-3-(p-tolyl)-1,4-pentadiene (**3d**). ^{1}H NMR: δ 7.58-7.15 (m, 14H), 6.26 (d, 1H, J = 9.2 Hz), 6.18 (d, 1H, J = 10.6 Hz), 4.84 (t, 1H, J = 10.0 Hz), 2.33 (s, 3H). ^{13}C NMR: δ 138.5, 137.6, 136.7, 136.6, 133.5, 132.8, 129.5, 129.2, 128.9, 128.8, 128.3, 127.8, 127.1, 126.5, 45.2, 21.0. Anal. Calcd for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.31. Found: C, 76.10; H, 5.40.

1,5-dichloro-3-(4-cyanophenyl)-1,5-diphenyl-1,4-pentadiene (**3e**). *E,Z*-isomer (40%): ^{1}H NMR: δ7.62-7.23 (m, 14H), 6.23 (d, 1H, J = 9.0 Hz), 6.15 (d, 1H, J = 10.4 Hz), 4.91 (t, 1H, J = 9.8 Hz). ^{13}C NMR: δ146.8, 137.0, 136.3, 134.9, 134.3, 132.6, 129.2, 128.5, 128.4, 128.0, 127.5, 126.5, 125.9, 118.6, 110.8, 45.6. *Z,Z*-isomer (60%): ^{1}H NMR: δ 7.64-7.22 (m, 14H), 6.31 (d, 2H, J = 8.9 Hz), 5.49 (t, 1H, J = 8.9 Hz). ^{13}C NMR: δ146.7, 137.2, 135.6, 132.6,129.1, 128.4, 128.2, 126.6, 125.8, 118.7, 110.7, 45.8. Anal. Calcd for $C_{24}H_{17}Cl_2N$: C, 73.85; H, 4.39; N, 3.59. Found: C, 73.63; H, 4.42; N, 3.72.

1,5-dichloro-3-phenyl-1,5-di(p-tolyl)-1,4-pentadiene (**3f**). ^{1}H NMR: δ7.48-7.12 (m, 13H), 6.22 (d, 1H, J = 9.2 Hz), 6.14 (d, 1H, J = 10.6 Hz), 4.87 (t, 1H, J = 10.0 Hz), 2.36(s, 3H), 2.34(s, 3H). ^{13}C NMR: δ141.7, 138.8, 134.9, 133.7, 133.1, 129.0, 128.8, 128.7, 127.3, 126.8, 126.5, 45.6, 21.3, 21.1. Anal. Calcd for $C_{25}H_{22}Cl_2$: C, 76.34; H, 5.64. Found: C, 76.16; H, 5.71.

1,5-dichloro-3-(4-fluorophenyl)-1,5-di(tolyl)-1,4-pentadiene (**3g**). ^{1}H NMR: δ7.46 (d, 2H, J = 8.1 Hz), 7.31 (d, 2H, J = 8.1 Hz), 7.22-6.95 (m, 8H), 6.19 (d, 1H, J = 9.0 Hz), 6.10 (d, 1H, J = 10.5 Hz), 4.84 (t, 1H, J = 9.8 Hz). ^{13}C NMR: δ163.7, 159.8, 139.0, 137.4, 134.7, 133.9, 133.7, 133.3, 129.0, 128.8, 128.6, 126.5, 126.4, 115.7, 44.9, 21.3, 21.1. Anal. Calcd for $C_{25}H_{21}Cl_2F$: C, 73.00; H, 5.15. Found: C, 72.83; H, 5.29.

1,5-dichloro-1,3,5-tri(p-tolyl)-1,4-pentadiene (**3h**). ^{1}H NMR: δ7.45(d, 2H, J = 8.2 Hz), 7.33 (d, 2H, J = 8.2 Hz), 7.18-7.11 (m, 8H), 6.21 (d, 1H, J = 9.1 Hz), 6.13 (d, 1H, J = 10.5 Hz), 4.84 (t, 1H, J = 9.9 Hz), 2.35-2.31(overlap, 9H). ^{13}C NMR: δ138.8, 138.7, 136.4, 134.9, 133.9, 133.5, 132.8, 129.5, 128.9, 128.7, 127.1, 127.0, 126.4, 45.2, 21.3, 21.0. Anal. Calcd for $C_{26}H_{24}Cl_2$: C, 76.66; H, 5.94. Found: C, 76.62; H, 6.08.

1,5-dichloro-1,3,5-tri(4-fluorophenyl)-1,4-pentadiene (**3i**). ^{1}H NMR: δ7.55-7.00 (m, 12H), 6.15 (m, 2H), 4.78 (t, 1H, J = 9.7 Hz). ^{13}C NMR: δ165.0, 164.9, 163.8, 161.1,

160.9, 159.9, 138.9, 133.5, 132.9, 132.7, 132.3, 130.7, 130.6, 128.9, 128.7, 128.5, 128.3, 127.2, 115.9, 115.6, 115.5, 115.3, 115.2, 44.9. Anal. Calcd for $C_{23}H_{15}Cl_2F_3$: C, 65.89; H, 3.61. Found: C, 66.13; H, 3.74.

1,5-dichloro-1,5-di(4-fluorophenyl)-3-(p-tolyl)-1,4-pentadiene (**3j**). ^{1}H NMR: δ 7.55-6.99 (m, 12H), 6.17 (m, 2H), 4.76 (t, 1H, J = 9.9 Hz), 2.33 (s, 3H). ^{13}C NMR: δ 165.0, 164.8, 161.0, 160.8, 138.2, 136.8, 133.8, 132.8, 132.4, 131.8, 130.8, 130.7, 129.6, 129.3, 128.5, 128.3, 127.7, 127.0, 115.5, 115.4, 115.2, 115.1, 45.3, 21.0. Anal. Calcd for $C_{24}H_{18}Cl_2F_2$: C, 69.41; H, 4.37. Found: C, 69.64; H, 4.49.

Representative procedure for the syntheses of 1,3,5-triaryl-1,5-dibromo-1,4-pentadienes (**4a-4j**). 4-Fluorobenzaldehyde (0.52 g, 4.2 mmol) and phenylacetylene (0.86 g, 8.4 mmol) were placed in a dry argon-flushed 50 mL round-bottomed flask equipped with a stirring bar and dissolved in 20 mL dry CH_2Cl_2. Boron tribromide (4.5 mmol, 4.5 mL of a 1.0 M CH_2Cl_2 solution) was added via syringe at –40 ^{o}C. The solution immediately turned purple. It was allowed to stir for 4 hrs at –40 ^{o}C, then hydrolyzed with water and extracted with hexanes. The organic layer was seperated and dried over anhydrous $MgSO_4$. The product was isolated by flash column chromatography.

1,5-Dibromo-3-(4-fluorophenyl)-1,5-diphenyl-1,4-pentadiene (4a). ^{1}H NMR: δ 7.58-7.00 (m, 14H), 6.40 (d, 2H, J = 8.9 Hz), 5.31 (t, 1H, J = 8.9 Hz). ^{13}C NMR: δ 163.8, 159.8, 139.4, 136.5, 130.7, 129.0, 128.9, 128.3, 127.7, 127.3, 115.8, 115.5, 50.7. Anal. Calcd for $C_{23}H_{17}Br_2F$: C, 58.50 ; H, 3.63. Found: C, 58.41 ; H, 3.73.

1,5-Dibromo-3-(4-chlorophenyl)-1,5-diphenyl-1,4-pentadiene (4b). *Z,Z*-isomer: ^{1}H NMR: δ 7.55-7.23 (m, 14H), 6.37 (d, 2H, J = 8.8 Hz), 5.30 (t, 1H, J = 8.8 Hz). ^{13}C NMR: δ 139.4, 132.9, 130.5, 129.0, 128.9, 128.4, 127.7, 50.9. *E,Z*-isomer (2% isolated): ^{1}H NMR: δ 7.53-7.16 (m, 14H), 6.39 (d, 1H, J = 10.3 Hz), 6.30 (d, 1H, J = 9.0 Hz), 4.73 (t,

1H, J = 9.6 Hz). ^{13}C NMR: δ139.5, 139.2, 138.1, 132.8, 132.3, 130.4, 129.0, 128.6, 128.3, 127.9, 126.8, 123.5, 48.8. Anal. Calcd for $C_{23}H_{17}Br_2Cl$: C, 56.53; H, 3.51. Found: C, 56.18; H, 3.50.

1,5-Dibromo-1,5-diphenyl-3-(p-tolyl)-1,4-pentadiene (4c). ^{1}H NMR: δ7.58-7.14 (m, 14H), 6.43 (d, 2H, J = 8.9 Hz), 5.30 (t, 1H, J = 8.9 Hz), 2.33 (s, 3H). ^{13}C NMR: δ139.6, 137.8, 136.5, 131.2, 129.5, 128.7, 128.2, 127.7, 127.3, 126.8, 51.0, 21.0. Anal. Calcd for $C_{24}H_{20}Br_2$: C, 61.56; H, 4.31. Found: C, 61.83; H, 4.35.

1,5-Dibromo-1,5-diphenyl-3-(o-tolyl)-1,4-pentadiene (4d). ^{1}H NMR: δ7.54-7.14 (m, 14H), 6.44 (d, 2H, J = 8.7 Hz), 5.34 (t, 1H, J = 8.7 Hz), 2.52 (s, 3H). ^{13}C NMR: δ 140.2, 139.4, 136.5, 131.5, 130.8, 128.7, 128.2, 127.7, 127.0, 126.8, 126.5, 126.4, 48.8, 20.1. Anal. Calcd for $C_{24}H_{20}Br_2$: C, 61.56; H, 4.31. Found: C, 61.27; H, 4.42.

1,5-Dibromo-3-(4-nitrophenyl)-1,5-diphenyl-1,4-pentadiene (4e). ^{1}H NMR: δ8.18-7.31 (m, 14H), 6.44 (d, 2H, J = 8.8 Hz), 5.42 (t, 1H, J = 8.8 Hz). ^{13}C NMR: δ148.2, 146.8, 138.9, 129.3, 129.1, 128.6, 128.4, 127.7, 124.0, 51.3. Anal. Calcd for $C_{23}H_{17}Br_2NO_2$: C, 55.34; H, 3.43; N, 2.81. Found: C, 55.60; H, 3.53; N, 2.87.

1,5-Dibromo-1,5-di(p-tolyl)-3-(4-fluorophenyl)-1,4-pentadiene (4f). ^{1}H NMR: δ7.46-6.96 (m, 12H), 6.35 (d, 2H, J = 8.9 Hz), 5.30 (t, 1H, J = 8.9 Hz), 2.31 (s, 6H). ^{13}C NMR: δ 163.6, 159.7, 138.8, 136.5, 129.8, 128.9, 128.8, 127.5, 127.3, 115.8, 115.3, 50.6, 21.1. Anal. Calcd for $C_{25}H_{21}Br_2F$: C, 60.02; H, 4.23. Found: C, 60.33; H, 4.52.

1,5-Dibromo-1,5-di(p-tolyl)-3-(4-bromophenyl)-1,4-pentadiene (4g). ^{1}H NMR: δ 7.46-7.06 (m, 12H), 6.33 (d, 2H, J = 8.9 Hz), 5.26 (t, 1H, J = 8.9 Hz), 2.32 (s, 6H). ^{13}C NMR: δ139.9, 138.9, 136.5, 131.8, 129.5, 128.9, 127.5, 120.7, 50.8, 21.1. Anal. Calcd for $C_{25}H_{21}Br_3$: C, 53.51; H, 3.77. Found: C, 53.21 ; H, 3.99.

1,5-Dibromo-1,5-di(4-chlorophenyl)-3-(4-fluorophenyl)-1,4-pentadiene (4h). ^{1}H NMR: δ7.51-7.00 (m, 12H), 6.39 (d, 2H, J = 8.9 Hz), 5.26 (t, 1H, J = 8.9 Hz). ^{13}C NMR: δ 163.8, 159.9, 137.7, 136.1, 134.8, 131.0, 128.9, 128.8, 128.4, 126.1, 115.9, 115.6, 50.7. Anal. Calcd for $C_{23}H_{15}Br_2Cl_2F$: C, 51.05; H, 2.79. Found: C, 51.37; H, 2.65.

1,5-Dibromo-1,5-di(4-chlorophenyl)-3-(4-bromophenyl)-1,4-pentadiene (4i). ^{1}H NMR: δ7.49-7.20 (m, 12H), 6.37 (d, 2H, J = 8.9 Hz), 5.23 (t, 1H, J = 8.9 Hz). ^{13}C NMR: δ139.4, 137.6, 134.8, 131.9, 130.5, 129.1, 128.9, 128.4, 126.4, 121.0, 50.9. Anal. Calcd for $C_{23}H_{15}Br_3Cl_2$: C, 45.89; H, 2.51. Found: C, 46.11; H, 2.66.

1,5-Dibromo-1,5-di(4-chlorophenyl)-3-(p-tolyl)-1,4-pentadiene (4j). ^{1}H NMR: δ7.46-7.16 (m, 12H), 6.43 (d, 2H, J = 8.7 Hz), 5.31 (t, 1H, J = 8.7 Hz), 2.51 (s, 3H). ^{13}C NMR: δ139.7, 137.8, 136.4, 134.6, 131.8, 128.9, 128.3, 126.9, 126.5, 125.3, 48.8, 20.2. Anal. Calcd for $C_{24}H_{18}Br_2Cl_2$: C, 53.67; H, 3.38. Found: C, 53.92; H, 3.45.