Intramolecular Cyclotrimerization of Triynes Catalyzed by *N*-Heterocyclic Carbene-CoCl₂ or -FeCl₃/Zn

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Supporting Information

General. NMR spectra were recorded in CDCl₃ at 600, 500 and 270 MHz for ¹H and 150, 125 and 67.5 MHz for ¹³C, respectively, on JEOL JNM-ECA600, 500 and -EX270 spectrometers. Chemical shifts are reported in parts per million (ppm, δ) relative to Me₄Si (δ 0.00), residual CHCl₃ (δ 7.26 for ¹H NMR), or CDCl₃ (δ 77.0 for ¹³C NMR). IR spectra were recorded on an FT-IR spectrometer (HITACHI 270-30). All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere.

Imidazolium salts, i.e., 1,3-bis(2,6-diisopropylphenyl)-3*H*-imidazol-1-ium chloride and 1,3-bis(2,4,6-trimethylphenyl)-3*H*-imidazol-1-ium chloride were prepared from the corresponding amines according to the reported procedures.¹

Dry solvent [tetrahydrofuran (THF)] was purchased from Kanto Chemicals. Other chemicals are commercially available, unless otherwise indicated, and were used as received.

Procedure for the Cyclotrimerization of Triynes **1** to Annulated Benzenes **2** Catalyzed by Imidazolium Carbene-CoCl₂ reagent in the Presence of Zn Powder

To a mixture of anhydrous CoCl₂ (13.0 mg, 0.1 mmol) and THF (2 mL) was added a solution of 1,3-bis(2,6-diisopropylphenyl)-3*H*-imidazol-1-ium carbene **3a** (0.24 mmol) in THF (2 mL), prepared from 1,3-bis(2,6-diisopropylphenyl)-3*H*-imidazol-1-ium chloride (102 mg, 0.24 mmol) and *n*-BuLi (0.152 mL, 1.58 M in hexanes, 0.24 mmol) in THF (2 mL), at 0 °C to give a clear dark green solution as a solution of catalyst precursor.

To a suspension of triyne **1** (1.0 mmol) and Zn powder (6.5 mg, 0.1 mmol) in THF (1 mL) was added a solution of catalyst precursor involving **3a** and CoCl₂ (prepared above, 0.4 ~ 2 mL, 0.01 ~ 0.05 mmol, 1 ~ 5 mol%) at room temperature. The resulting mixture was stirred for 12 ~ 48 h at room temperature ~ THF-reflux temperature. After being cooled to room temperature, the mixture was filtered through a pad of Celite with ether and saturated aqueous NH₄Cl (10 mL) was added. The mixture was extracted with ether (2 x 10 mL), washed with brine, dried over MgSO₄, concentrated *in vacuo*. The residue was chromatographed on silica gel to give the corresponding annulated benzene **2**.

Procedure for the Cyclotrimerization of Triynes **1** to Annulated Benzenes **2** Catalyzed by Imidazolium Carbene-FeCl₃ reagent in the Presence of Zn Powder

To a mixture of anhydrous FeCl_3 (16.2 mg, 0.1 mmol) and THF (2 mL) was added a solution of 1,3-bis(2,6-diisopropylphenyl)-3*H*-imidazol-1-ium carbene **3a** (0.12 mmol) in THF (2 mL), prepared from 1,3-bis(2,6-diisopropylphenyl)-3*H*-imidazol-1-ium chloride (51.0 mg, 0.12 mmol) and *n*-BuLi (0.076 mL, 1.58 M in hexanes, 0.12 mmol) in THF, at 0 °C to give a clear brown solution as a solution of catalyst precursor.

To a suspension of triyne **1** (1.0 mmol) and Zn powder (6.5 mg, 0.1 mmol) in THF (1 mL) was added a solution of catalyst precursor involving **3a** and FeCl_3 (prepared above, 0.8 ~ 2 mL, 0.02 ~ 0.05 mmol, 2 ~ 5 mol%) at room temperature. The resulting mixture was stirred for 24 ~ 48 h at room temperature ~ THF-reflux temperature. After being cooled to room temperature, the mixture was filtered through a pad of Celite with ether and saturated aqueous NH_4Cl (10 mL) was added. The mixture was extracted with ether (2 x 10 mL), washed with brine, dried over MgSO_4 , concentrated *in vacuo*. The residue was chromatographed on silica gel to give the corresponding annulated benzene **2**.

^1H NMR (500 MHz, CDCl_3) δ 7.15 (s, 2H, Ar), 5.13 (s, 4H, ArCH_2O), 5.04 (s, 4H, ArCH_2O).

^{13}C NMR (125 MHz, CDCl_3) δ 138.6, 132.3, 119.9, 73.4, 72.2.

IR (KBr): 2854, 1464, 1386, 1038, 1018 cm^{-1} .

Mp 83 - 85 °C.

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.06; H, 6.21. Found: C, 73.70; H, 6.09.

^1H NMR (500 MHz, CDCl_3) δ 7.29 (s, 1H, Ar), 5.17 (s, 2H, ArCH_2O), 5.14 (s, 2H, ArCH_2O), 5.03 (s, 4H, ArCH_2O), 0.29 (s, 9H, TMS).

^{13}C NMR (67.5 MHz, CDCl_3) δ 143.9, 138.2, 133.4, 131.9, 131.5, 125.2, 73.9, 73.5, 72.3, 71.9, - 0.98.

IR (neat): 2956, 2895, 2855, 1767, 1251, 1059 cm^{-1} .

Mp 116 - 117 °C.

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Si}$: C, 66.62; H, 7.74. Found: C, 66.63; H, 7.68.

^1H NMR (500 MHz, CDCl_3) δ 7.11 (s, 1H, Ar), 5.12 (s, 4H, ArCH_2O), 5.02 (s, 4H, ArCH_2O), 4.66 (s, 2H, ArCH_2OTBS), 0.93 (s, 9H, *t*-Bu), 0.10 (s, 6H, $\text{Si}(\text{CH}_3)_2$).

^{13}C NMR (125 MHz, CDCl_3) δ 139.1, 136.3, 134.3, 132.4, 130.9, 117.6, 73.4, 72.7, 72.14, 72.09, 63.6, 25.9, 18.4, - 5.4.

IR (KBr): 2954, 2930, 2857, 1762, 1466, 1348, 1007, 839 cm^{-1} .

Mp 84 - 85 °C.

Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_3\text{Si}$: C, 66.62; H, 8.55. Found: C, 66.99; H, 8.48.

^1H NMR (500 MHz, CDCl_3) δ 6.98 – 7.22 (m, 10H, Ph), 5.14 (s, 4H, ArCH_2O), 4.99 (s, 4H, ArCH_2O).

^{13}C NMR (125 MHz, CDCl_3) δ 138.7, 138.4, 134.1, 131.2, 129.4, 127.9, 126.8, 73.6, 72.7.

IR (KBr): 2922, 2847, 1446, 1429, 1352, 1063, 1043 cm^{-1} .

Mp 188 - 193 $^\circ\text{C}$.

Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_2$: C, 84.05; H, 5.77. Found: C, 83.71; H, 5.76.

^1H NMR (500 MHz, CDCl_3) δ 5.11 (s, 4H, ArCH_2O), 5.02 (s, 4H, ArCH_2O), 2.49 - 2.53 (m, 4H, ArCH_2CH_2), 1.37 - 1.50 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.95 (t, 6H, $J = 7.0$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$).

^{13}C NMR (125 MHz, CDCl_3) δ 138.3, 133.3, 129.3, 73.0, 72.7, 32.7, 29.6, 23.0, 13.9.

IR (neat): 2956, 2930, 2866, 1461, 1056 cm^{-1} .

Mp 93 - 95 $^\circ\text{C}$.

Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2$: C, 78.79; H, 9.55. Found: C, 78.54; H, 9.70.

^1H NMR (500 MHz, CDCl_3) δ 5.17 (s, 4H, ArCH_2O), 4.95 (s, 4H, ArCH_2O), 0.40 (s, 18H, TMS).

^{13}C NMR (125 MHz, CDCl_3) δ 145.6, 138.9, 132.4, 74.8, 71.2, 3.6.

IR (neat): 2950, 2900, 2855, 1728, 1251, 1059 cm^{-1} .

Mp 134 - 136 $^\circ\text{C}$.

Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{Si}_2$: C, 62.69; H, 8.55. Found: C, 62.80; H, 8.48.

^1H NMR (500 MHz, CDCl_3) δ 7.10 (d, 1H, $J = 8.0$ Hz, Ar), 7.02 (d, 1H, $J = 8.0$ Hz, Ar), 5.33 (m, 1H, $\text{ArCH}(\text{CH}_3)$), 5.11 (d, 1H, $J = 12.0$ Hz, ArCH_2O), 4.99 (d, 1H, $J = 12.0$ Hz, ArCH_2O), 4.22 (q, 2H, $J = 6.5$ Hz, CH_2CH_3), 4.20 (q, 2H, $J = 6.5$ Hz, CH_2CH_3), 3.62 (d, 1H, $J = 16.5$ Hz, ArCH_2C), 3.59 (d, 1H, $J = 16.5$ Hz, ArCH_2C), 3.55 (d, 1H, $J = 16.5$ Hz, ArCH_2C), 3.46 (d, 1H, $J = 16.5$ Hz, ArCH_2C), 1.50 (d, 3H, $J = 6.0$ Hz, $\text{CH}(\text{CH}_3)$), 1.27 (t, 3H, $J = 6.5$ Hz, CH_2CH_3), 1.25 (t, 3H, $J = 6.5$ Hz, CH_2CH_3).

^{13}C NMR (125 MHz, CDCl_3) δ 171.4 (2C), 139.7, 138.8, 138.1, 132.9, 123.2, 119.6, 79.4, 72.2, 61.7 (2C), 60.6, 39.8, 38.2, 20.6, 13.93, 13.91.

IR (KBr): 2978, 1746, 1733, 1715, 1467, 1450, 1218, 1240, 1184, 1157, 1070 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_5$: C, 67.91; H, 6.97. Found: C, 67.64; H, 7.06.

^1H NMR (600 MHz, CDCl_3) δ 7.14 (s, 1H, Ar), 5.16 (s, 2H, ArCH_2O), 5.10 (s, 2H, ArCH_2O), 5.01 (brs, 4H, ArCH_2O), 4.65 (d, 2H, $J = 5.4$ Hz, ArCH_2OH), 2.06 (t, 1H, $J = 5.4$ Hz, OH).

^{13}C NMR (150 MHz, CDCl_3) δ 139.3, 137.0, 133.7, 132.6, 131.5, 118.4, 73.3, 72.5, 72.14, 72.08, 63.3.

IR (KBr): 3400, 2855, 1640, 1618, 1086, 1040 cm^{-1} .

Mp 135 - 137 $^\circ\text{C}$.

Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$: C, 68.74; H, 6.29. Found: C, 68.49, H, 6.41.

^1H NMR (500 MHz, CDCl_3) δ 7.24 – 7.29 (m, 6H, Ph), 7.13 – 7.16 (m, 4H, Ph), 5.20 (d, 2H, $J = 14.0$ Hz, ArCH_2O), 5.17 (d, 2H, $J = 14.0$ Hz, ArCH_2O), 5.03 – 5.11 (m, 8H, ArCH_2O), 4.72 (d, 2H, $J = 12.0$ Hz, ArCH_2O), 4.64 (d, 2H, $J = 12.0$ Hz, ArCH_2O), 4.32 (d, 2H, $J = 11.5$ Hz, ArCH_2OBn), 4.29 (d, 2H, $J = 11.5$ Hz, ArCH_2OBn), 4.12 (d, 2H, $J = 11.0$ Hz, PhCH_2O), 4.08 (d, 2H, $J = 11.0$ Hz, PhCH_2O).

^{13}C NMR (125 MHz, CDCl_3) δ 139.7, 138.2, 137.5, 132.5, 131.9, 130.0, 129.0, 128.3, 127.74, 127.71, 73.3, 73.2, 73.1, 72.8, 72.2, 67.6.

IR (KBr): 3057, 3032, 2889, 2855, 175, 1767, 1458, 1450, 1350, 1087, 1048 cm^{-1} .

Mp 150 - 159 $^\circ\text{C}$.

Anal. Calcd for $\text{C}_{36}\text{H}_{34}\text{O}_6$: C, 76.85; H, 6.09. Found: C, 76.87, H, 6.06.

References

- (a) Arduengo, A. J., III. US patent 5,077,414, 1991. (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.