Supporting Information

The Reaction of Diaryl-1,2-diones with Triphenylphosphine and Diethyl Azodicarboxylate Leading to N, N-Dicarboethoxy Monohydrazones via a Novel Rearrangement

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General

All reactions were conducted in oven-dried glassware sealed with rubber septa under a positive pressure of deoxygenated argon from a manifold. Solvents used for the experiments were distilled or dried as specified. Diethyl azodicarboxylate (DEAD) and benzil were purchased from Aldrich and used as received. Diaryl-1,2-diones were prepared from the corresponding aldehydes by thiamine catalyzed benzoin condensation and subsequent oxidation.¹ All other reagents were purchased from local suppliers and used without purification. All reactions were monitored by TLC, visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (100-200 mesh).

Melting points were recorded on a Buchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 (¹H) and 75 (¹³C) MHz respectively on a Bruker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (¹H) or CDCl₃ (¹³C) as internal standards. IR spectra were recorded on Bomem MB series FT-IR spectrometer; absorbencies are reported in cm⁻¹. High resolution mass spectra were obtained using Autospec M mass spectrometer. Elemental analyses were performed on a Perkin Elmer-2400 elemental analyzer.

General experimental procedure

To a stirred solution of diaryl-1,2-dione (0.5mmol) and diethyl azodicarboxylate (104mg, 0.6mmol) in anhydrous THF (10 mL) under an atmosphere of Ar, triphenylphosphine (157mg, 0.6mmol) was added and the reaction mixture was stirred at room temperature till the reaction is complete (TLC). Solvent was removed on a

rotavap, residue column chromatographed on silica gel using 9:1 hexanes-ethyl acetate as eluent to afford the respective product.

Hydrazone **6a**

White crystals. **Mp** 125-127 °C.

IR (KBr) ν_{max} : 2991, 1798, 1710, 1680, 1592, 1449, 615 cm^{-1} .

^1H NMR δ : 1.26 (t, $J = 7.17$ Hz, 6H), 4.19 (q, $J = 7.17$ Hz, 4H), 7.42-7.62 (m, 5H), 7.81 (d, $J = 7.44$ Hz, 2H), 7.89 (d, $J = 7.53$ Hz, 2H).

^{13}C NMR δ : 14.1, 63.5, 128.4, 128.8, 129.0, 129.5, 131.9, 132.6, 133.9, 134.8, 150.8, 175.1, 193.2.

Elemental anal. calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5$: C, 65.21, H, 5.47, N, 7.60. Found: C, 64.76, H, 5.02, N, 7.67.

Hydrazone **6b** (oil)

IR (KBr) ν_{max} : 2985, 2929, 2254, 1786, 1747, 1674, 1602, 1463, 1375, 1253, 1176, 1105, 1008, 900 cm^{-1}

^1H NMR δ : 1.28 (t, $J = 6.99$ Hz, 6H), 2.39 (s, 6H), 4.19 (q, $J = 7.00$ Hz, 4H), 7.20-7.27 (m, 4H), 7.68 (d, $J = 8.01$ Hz, 2H), 7.77 (d, $J = 7.92$ Hz, 2H)

^{13}C NMR δ : 14.1, 14.2, 21.6, 21.8, 63.3, 64.0, 128.3, 129.3, 129.6, 129.9, 131.6, 143.1, 145.8, 150.8, 175.0, 192.8.

HRMS for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_5$: calcd. (M+H): 397.1763, found: 397.1773.

Hydrazone **6c** (oil)

IR (KBr) ν_{max} : 3545, 3022, 2403, 1757, 1726, 1678, 1600, 1508, 1371, 1267, 1093, 1008, 925 cm^{-1} .

^1H NMR δ : 1.27 (t, $J = 7.12$ Hz, 6H), 4.21 (q, $J = 7.12$ Hz, 4H), 7.11-7.16 (m, 4H), 7.80 (d, $J = 5.40$ Hz, 2H), 7.94 (d, $J = 7.78$ Hz, 2H).

^{13}C NMR δ : 14.0, 63.6, 116.1, 116.2, 116.4, 116.5, 127.9, 130.3, 130.6, 132.4, 150.8, 163.7, 165.0, 167.2, 168.5, 173.3, 191.4.

HRMS for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_5\text{F}_2$: FAB calcd. (M+H): 405.1184, found: 405.1783.

Hydrazone **6d** (oil)

IR (KBr) ν_{max} : 2985, 2256, 1759, 1749, 1573, 1514, 1404, 1373, 1251, 1130, 918 cm^{-1}

^1H NMR δ : 1.27 (t, $J = 7.08$ Hz, 6H), 4.22 (q, $J = 7.08$ Hz, 4H), 7.70-7.76 (m, 4H), 7.92 (d, $J = 8.16$ Hz, 2H), 8.01 (d, $J = 8.11$ Hz, 2H).

^{13}C NMR δ : 14.0, 63.9, 121.4, 121.6, 125.0, 125.3, 125.9, 126.1, 128.7, 129.8, 134.1, 134.5, 135.5, 135.9, 136.2, 136.4, 150.7, 171.7, 191.7.

HRMS for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_5\text{F}_6$: calcd. (M+H): 505.1198, found: 505.1162.

Hydrazone **6e** (oil)

IR (KBr) ν_{max} : 3302, 2983, 2357, 1750, 1728, 1591, 1460, 1408, 1321, 1244, 1031, 937 cm^{-1} .

^1H NMR δ : 1.28 (t, $J = 7.10$ Hz, 6H), 4.21 (q, $J = 7.10$ Hz, 4H), 7.39-7.57 (m, 3H), 7.57 (d, $J = 8.34$ Hz, 1H), 7.67 (dd, $J_1 = 8.34$, $J_2 = 1.99$ Hz, 1H), 7.94 (d, $J = 1.99$ Hz, 1H).

^{13}C NMR δ : 14.5, 62.7, 126.9, 127.9, 128.2, 128.6, 128.9, 129.8, 130.6, 131.8, 132.7, 133.2, 133.6, 136.1, 161.1, 162.9, 181.3.

HRMS for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_5\text{Cl}_4$: calcd. (M^+): 503.9813, found: 503.9735.

Hydrazone **6f**

White crystalline solid, **Mp.** 162-164 °C

IR (KBr) ν_{max} : 3701, 2704, 2048, 1784, 1653, 1558, 1411, 1261, 1095, 856 cm^{-1} .

^1H NMR δ : 1.28 (t, $J = 7.08$ Hz, 6H), 4.23 (q, $J = 7.08$ Hz, 4H), 7.07-7.12 (m, 2H), 7.27 (broad s, 1H), 7.61 (d, $J = 4.73$ Hz, 1H), 7.68 (d, $J = 3.73$ Hz, 1H), 7.81 (d, $J = 4.74$ Hz, 1H).

^{13}C NMR δ : 14.2, 63.6, 128.1, 128.4, 132.4, 133.4, 133.8, 135.9, 136.2, 136.7, 136.9, 140.7, 150.8, 168.3, 183.1.

HRMS for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_5\text{S}_2$: calcd. (M^+): 380.0501, found: 380.0546.

Hydrazone **6g** (oil)

IR (KBr) ν_{max} : 3020, 2401, 1751, 1724, 1589, 1490, 1379, 1255, 1097, 1006, 881 cm^{-1} .

^1H NMR δ : 1.30 (t, $J = 6.99$ Hz, 6H), 4.22 (q, $J = 6.99$ Hz, 4H), 6.80 (d, $J = 8.20$ Hz, 2H), 7.14 (d, $J = 8.37$ Hz, 2H), 7.43 (d, $J = 8.37$ Hz, 2H), 7.55 (d, $J = 8.20$ Hz, 2H).

^{13}C NMR δ : 13.8, 64.1, 122.4, 124.4, 127.6, 127.8, 127.9, 128.2, 129.5, 131.3, 132.0, 134.4, 142.2, 153.2, 169.3, 196.2.

HRMS for $C_{20}H_{18}N_2O_5Br_2$: calcd. (M^+): 523.9581, found: 523.9521.

Hydrazone **6h** (oil)

IR (KBr) $\nu_{\max}$: 3020, 2401, 1751, 1724, 1589, 1490, 1379, 1255, 1097, 1006, 881 cm^{-1} .

^1H NMR δ : 1.28 (t, $J = 7.26$ Hz, 6H), 4.20 (q, $J = 7.26$ Hz, 4H), 6.87 (d, $J = 6.86$ Hz, 2H), 7.19 (d, $J = 7.20$ Hz, 2H), 7.27 (d, $J = 7.20$ Hz, 2H), 7.39 (d, $J = 6.86$ Hz, 2H).

^{13}C NMR δ : 14.2, 64.1, 127.5, 128.0, 128.7, 129.3, 129.6, 129.8, 130.4, 134.3, 134.6, 136.4, 153.6, 170.8, 190.0.

HRMS for $C_{20}H_{18}N_2O_5Br_2$: calcd. (M^+): 523.9581, found: 523.9521.

Hydrazone **6i**

Brown crystalline solid Mp. 88-90 $^{\circ}C$

IR (KBr) $\nu_{\max}$: 2989, 1764, 1737, 1662, 1600, 1516, 1448, 1369, 1292, 1271, 1193, 1003, 949 cm^{-1} .

^1H NMR δ : 1.35 (t, $J = 7.08$ Hz, 6H), 4.37 (q, $J = 7.08$ Hz, 4H), 7.37-7.44 (m, 2H), 7.54 (t, $J = 7.60$ Hz, 1H), 7.66 (t, $J = 6.54$ Hz, 1H), 7.97 (t, $J = 8.34$ Hz, 2H), 8.08 (d, $J = 7.81$ Hz, 1H), 8.29 (d, $J = 7.89$ Hz, 1H).

^{13}C NMR δ : 14.2, 63.9, 123.3, 12.5, 123.9, 127.9, 128.6, 129.2, 129.4, 130.7, 130.9, 131.7, 131.8, 135.1, 136.3, 151.8, 151.9, 162.5, 179.8.

HRMS for $C_{20}H_{18}N_2O_5$: calcd. (M^+): 366.1215, found: 366.1211.

Oxadiazoline **9** (oil)

IR (KBr) $\nu_{\max}$: 2990, 1758, 1709, 1691, 1449, 1377, 1336, 1284, 1228 cm^{-1}

^1H NMR δ : 1.31 (t, $J = 7.08$ Hz, 6H), 1.41 (t, $J = 7.08$ Hz, 3H), 1.91 (s, 3H), 4.23 (q, $J = 7.32$ Hz, 4H), 4.31 (q, $J = 5.91$ Hz, 2H)

^{13}C NMR δ : 14.1, 14.5, 21.0, 62.1, 62.4, 68.3, 96.7, 157.6, 165.8.

HRMS for $\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_6$: calcd. (M^+): 274.1165, found: 274.1118.

Ene-hydrazine **10**

Colourless crystalline solid Mp. 136-138 $^{\circ}\text{C}$

IR (KBr) $\nu_{\max}$: 3294, 2990, 1722, 1645, 1527, 1372, 1233 cm^{-1}

^1H NMR δ : 1.25 (t, $J = 6.75$ Hz, 3H), 1.32 (t, $J = 7.17$ Hz, 3H), 2.38- 2.48 (m, 2H), 2.78 (t, $J = 8.19$ Hz, 2H), 4.18- 4.33 (m, 4H), 6.3 (bs, 1H), 6.99 (bs, 1H), 7.14- 7.20 (m, 4H).

^{13}C NMR δ : 14.1, 14.5, 21.5, 27.1, 61.9, 62.7, 121.7, 126.4, 126.5, 127.5, 127.6, 128.0, 128.9, 136.2, 158.3.

Reference

1. Pavia, D. L.; Lampman, G. M.; Kriz, S. G.; Engel, R. G. In *Introduction to Organic Laboratory Techniques: A Microscale approach*, 3rd Ed., 1999, Saunders College Publishing, p. 307.