A Novel and Efficient Method for the Olefination of Carbonyl Compounds with Grignard Reagents in the Presence of Diethyl Phosphite

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Supporting Information

General: Tetrahydrofuran was distilled from sodium and benzophenone immediately prior to use. All reactions were carried out under a nitrogen atmosphere. Metallic magnesium and all other solvents were purchased from commercial source, without further purification before use. The flash column chromatography was carried out on Merck silica gel (300-400 mesh). 1H and 13C NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer as solutions in CDCl3. Chemical shifts in 1H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me4Si (TMS). Chemical shifts in 13C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.50 ppm). High-resolution mass spectra were obtained with a GCT-TOF instrument.

Materials: The other chemicals were purchased from Aldrich, Alfa or Acros chemical company and used thus, without further purification. Petroleum ether (PE) used refers to the 30-60°C boiling point fraction of petroleum.

General procedure for the synthesis of olefins: A solution of Grignard reagents in THF (0.5 M, 2.2 mL, 1.1 mmol) was added to a solution of carbonyl compounds (0.5 mmol) in dry THF (6 mL) under a nitrogen atmosphere at room temperature. The mixture was stirred for about 30 min. Then the diethyl phosphite (0.6 mmol) was added (the reaction was monitored by TLC). The reaction mixture was stirred for 3-5 h and then was quenched with water. The resulting mixture was extracted with diethyl ether (3×10 mL), and dried over anhydrous Na2SO4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded olefins (300-400 mesh, petroleum ether as eluent).

Buta-1,3-diene-1,1-diyldibenzene (entry 1) [1] The title compound was obtained according to the general procedure. Colourless oil; Yield: 90%; 1H NMR (400 MHz, CDCl3): δ: 7.38-7.17 (m, 10H), 6.71 (d, J = 11.1 Hz, 1H), 6.44 (td, J = 10.5 Hz, J = 16.9 Hz, 1H), 5.38 (d, J = 16.9 Hz, 1H), 5.11 (d, J = 10.1 Hz, 1H). 13C NMR (CDCl3, 75 MHz): δ: 143.59, 142.53, 140.09, 135.41, 130.87, 128.97, 128.64, 128.63, 128.04, 127.96, 127.84, 119.08. HRMS (EI+): calcd for C18H18O2 (M+): 266.1307; found: 266.1306.

4,4’-(buta-1,3-diene-1,1-diyl)bis(chlorobenzene) (entry 2) [1] The title compound was obtained according to the general procedure. Colourless oil; Yield: 83%; 1H NMR (300 MHz, CDCl3): δ: 7.37-7.11 (m, 8H), 6.67 (d, J = 11.0 Hz, 1H), 6.38 (td, J = 10.5 Hz, J = 16.8 Hz, 1H), 5.42 (dd, J = 0.9 Hz, J = 16.8 Hz, 1H), 5.18 (dd, J = 0.9 Hz, J = 10.1 Hz, 1H). 13C NMR (75 MHz, CDCl3): δ: 141.06, 140.59, 137.99, 134.75, 134.02, 132.16, 129.74, 129.66, 129.22, 129.03, 128.91, 120.35. HRMS (EI+): calcd for C16H12Cl2 (M+): 274.0316; found: 274.0316; HRMS(EI')+ calcd for C16H12Cl2 (M+): 266.1307; found: 266.1306.

4,4’-(buta-1,3-diene-1,1-diyl)bis(methoxybenzene) (entry 3) [1] The title compound was obtained according to the general procedure. Colourless oil; Yield: 95%; 1H NMR (400 MHz, CDCl3): δ: 7.24-7.11 (m, 8H), 6.94 (s, 1H), 6.82 (d, J = 8.7 Hz, 1H), 6.44 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 11.0 Hz, 1H), 6.46 (td, J = 10.4 Hz, J = 16.7 Hz, 1H), 5.34 (dd, J = 1.7 Hz, J = 16.7 Hz, 1H), 5.07 (dd, J = 1.8 Hz, J = 10.0 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H). 13C NMR (CDCl3, 100 MHz): δ: 159.63, 159.32, 142.84, 135.72, 135.55, 132.57, 132.08, 129.32, 127.17, 117.77, 113.98, 113.92, 55.75, 55.73. HRMS (EI+): calcd for C18H11O2Cl2 (M+): 360.0388; found: 360.0388.

(E)-1-(buta-1,3-dienyl)-4-methoxybenzene (entry 4) [1] The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; 1H NMR (300 MHz, CDCl3): δ: 7.34 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.67 (dd, J = 10.6 Hz, J = 15.3 Hz, 1H), 6.54-6.37 (m, 2H), 5.28 (d, J = 16.7 Hz, 1H), 5.11 (d, J = 9.6 Hz, 1H), 3.81 (s, 3H). 13C NMR (75 MHz, CDCl3): δ: 159.74, 137.84, 132.87, 130.39, 128.42, 128.12, 116.94, 114.53, 55.77. HRMS (EI+): calcd for C19H13O (M+): 260.0888; found: 260.0888.

(E)-5-buta-1,3-dienyl)-benzo[1,3]dioxole (entry 5) The title compound was obtained according to the general procedure. Colourless oil; Yield: 87%; 1H NMR (300 MHz, CDCl3): δ: 6.94 (s, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 6.62 (dd, J = 10.2 Hz, J = 15.4 Hz, 1H), 6.54 (d, J = 8.6 Hz, 2H), 5.54 (d, J = 15.4 Hz, 1H).

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IR (KBr) 3078, 2961, 2920, 1671, 1491, 1257, 1034, 930, 800, 669 cm⁻¹. HRMS (EI⁺): calcd for C₁₇H₁₇O₂ (M⁺): 276.1179, found: 276.1178.

1-(biphenyl)thiophene (entry 14) [vi] The title compound was obtained according to the general procedure. Colourless oil; Yield: 92%; ¹H NMR (300 MHz, CDCl₃): δ 7.45-7.52 (m, 4H), 7.30 (d, J = 1.8 Hz, 1H), 7.27 (d, J = 4.9 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 7.19 (d, J = 5.0 Hz, 1H), 7.12 (d, J = 1.1 Hz, 1H), 5.86 (s, 1H), 5.49 (s, 1H), 3.56 (s, 1H), 2.89 (s, 1H), 2.23 (s, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 154.67, 142.79, 139.57, 138.29, 137.15, 129.38, 128.63, 128.38, 128.09, 128.05, 127.72, 126.96, 126.58, 126.43, 114.68, 21.68. HRMS (EI⁺): calcd for C₁₇H₁₇S (M⁺): 272.1044, found: 272.1042.
2-cyclopentenylthiophene (entry 18) \(^{(9)}\) The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 7.27 (d, \(J = 8.6 \) Hz, 2H), 6.83 (d, \(J = 8.7 \) Hz, 2H), 6.32 (d, \(J = 15.8 \) Hz, 1H), 6.12 (td, \(J = 6.4 \) Hz, \(J = 15.7 \) Hz, 1H), 3.79 (s, 3H), 2.20 (p, \(J = 6.4 \) Hz, 2H), 1.08 (t, \(J = 7.4 \) Hz, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta \) 158.77, 139.50, 136.51, 132.07, 131.40, 129.87, 129.33, 128.47, 128.00, 127.87, 127.15, 114.41, 113.99, 113.75, 55.69, 48.64. HRMS (EI\(^+\)): calcld. for C\(_{12}\)H\(_{20}\)O\(_2\) (M\(^+\)): 224.0837, found: 224.0837.

2-Ethylidene-adamantane (entry 23) \(^{(10)}\) The title compound was obtained according to the general procedure. Colourless oil; Yield: 43%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 5.08 (q, \(J = 6.7 \) Hz, 1H), 2.84 (s, 1H), 2.32 (s, 1H), 1.94-1.67 (m, 12H), 1.55 (d, \(J = 6.7 \) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 148.50, 110.27, 40.95, 40.26, 39.17, 37.79, 32.03, 29.12, 12.54. HRMS (EI\(^+\)): calcld. for C\(_{16}\)H\(_{24}\)O\(_2\) (M\(^+\)): 244.1409 found: 244.1408.

1-methoxy-4-(1-(4-methoxyphenyl)-2-phenylvinyl)benzene (entry 24) \(^{(11)}\) The title compound was obtained according to the general procedure. Colourless solid; Yield: 81%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 7.44 (d, \(J = 7.3 \) Hz, 4H), 7.33 (t, \(J = 7.4 \) Hz, 4H), 7.26-7.21 (m, 2H), 6.96 (dd, \(J = 2.8 \) Hz, \(J = 12.0 \) Hz, 1H), 6.67 (dd, \(J = 2.7 \) Hz, \(J = 12.0 \) Hz, 1H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta \) 137.79, 133.28, 129.70, 129.14, 128.05, 126.85. HRMS (EI\(^+\)): calcld. for C\(_{20}\)H\(_{18}\)O\(_2\) (M\(^+\)): 294.1319, found: 294.1312.

1,2,3-triphenylprop-1-ene (entry 27) \(^{(12)}\) The title compound was obtained according to the general procedure. Colourless solid; Yield: 81%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 7.49 (d, \(J = 7.1 \) Hz, 2H), 7.36-7.15 (m, 13H), 7.12 (s, 1H, trans), 6.43 (s, 1H, cis), 4.13 (s, 2H, trans), 3.77 (s, 2H, cis). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta \) 142.83, 140.12, 139.43, 138.16, 130.79, 129.72, 129.50, 129.04, 128.84, 128.30, 127.76, 127.65, 126.94, 126.41, 47.40(cis), 36.53(trans). HRMS (EI\(^+\)): calcld. for C\(_{25}\)H\(_{20}\) (M\(^+\)): 378.1407, found: 378.1407.

2,4-diphenylbut-1-en-3-yne (entry 28) \(^{(13)}\) The title compound was obtained according to the general procedure. Colourless oil; Yield: 72%; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta \) 7.72 (d, \(J = 7.5 \) Hz, 2H), 7.53 (d, \(J = 3.8 \) Hz, 2H), 7.44-7.22 (m, 6H), 5.98 (s, 1H), 5.76 (s, 1H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta \) 137.72, 132.97, 132.14, 131.07, 129.68, 128.89, 128.83, 126.57, 123.56, 121.16, 91.26, 89.03. HRMS (EI\(^+\)): calcld. for C\(_{24}\)H\(_{21}\) (M\(^+\)): 344.1501, found: 344.1501.
1H and 13C NMR spectrums

entry 5
References