

SUPPORTING INFORMATION

Title: Heck Reactions of α - or β -Substituted Enol Ethers with Aryl Bromides Catalysed by a Tetracosphane/Palladium Complex – Direct Access to Acetophenone or 1-Arylpropanone Derivatives

Author(s): Ahmed Battace, Marie Feuerstein, Mhamed Lemhadri, Touriya Zair, Henri Doucet,* Maurice Santelli*

Ref. No.: O200700152

General

DMF analytical grade (99.8%) was not distilled before use. K_2CO_3 or $NaHCO_3$ 99+ were used. All reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. 1H (300 MHz) and ^{13}C (75 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shift (δ) are reported in ppm relative to $CDCl_3$. Flash chromatographies were performed on silica gel (230-400 mesh).

Preparation of the Pd-Tedicyp Catalyst

An over-dried 40-mL Schlenk tube equipped with a magnetic stirring bar, under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_5$ (4.2 mg, 11.6 μ mol) and Tedicyp (20 mg, 23.2 μ mol). 2.5 mL of anhydrous DMF were added, then the solution was stirred at room temperature for 10 min. This catalyst solution was used directly for the catalysed reactions.

2-(4-Acetylphenyl)-1-phenylethanone (2) (Table 1, Entry 3)

1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.3 Hz, 2 H), 7.92 (d, J = 8.3 Hz, 2 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.47 (dd, J = 8.3, 7.2 Hz, 2 H), 7.36 (d, J = 8.3 Hz, 2 H), 4.35 (s, 2 H), 2.58 (s, 3 H).

1-Phenyl-2-(4-trifluoromethylphenyl)-ethanone (3) (Table 1, Entry 4)

1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.3 Hz, 2 H), 7.62-7.57 (m, 3 H), 7.51-7.46 (m, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 4.29 (s, 2 H).

4-(2-Oxo-2-phenylethyl)-benzotrile (4) (Table 1, Entry 6)

1H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.3 Hz, 2 H), 7.64-7.58 (m, 3 H), 7.50 (d, J = 8.3 Hz, 2 H), 7.38 (d, J = 8.3 Hz, 2 H), 4.36 (s, 2 H).

2-(4-*tert*-Butylphenyl)-1-phenylethanone (5) (Table 1, Entry 8)

1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.3 Hz, 2 H), 7.59-7.54 (m, 1 H), 7.49-7.44 (m, 2 H), 7.35 (m, 2 H), 7.23 (m, 2 H), 4.26 (s, 2 H), 1.29 (s, 9 H).

2-(1-Naphthyl)-1-phenylethanone (7) (Table 1, Entry 10)

1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.2 Hz, 2 H), 7.89-7.86 (m, 2 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.61-7.56 (m, 1 H), 7.51-7.46 (m, 4 H), 7.41 (m, 1 H), 7.34 (d, J = 8.0 Hz, 1 H), 4.74 (s, 2 H).

1-Phenyl-2-*o*-tolyl-ethanone (8) (Table 1, Entry 12)

1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.3 Hz, 2 H), 7.61-7.56 (m, 1 H), 7.51-7.46 (m, 2 H), 7.22-7.14 (m, 4 H), 4.32 (s, 2 H), 2.27 (s, 3 H).

2-(2-Methoxyphenyl)-1-phenyl-ethanone (9) (Table 1, Entry 13)

1H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, J = 8.0 Hz, 2 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.29-7.19 (m, 1 H), 7.18 (d, J = 8.2 Hz, 1 H), 6.93 (t, J = 8.0 Hz, 1 H), 6.89 (d, J = 8.0 Hz, 1 H), 4.29 (s, 2 H), 3.79 (s, 3 H).

1-Phenyl-2-(2,4,6-trimethylphenyl)-ethanone (10) (Table 1, Entry 14)

1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.5 Hz, 2 H), 7.61-7.58 (m, 1 H), 7.53-7.48 (m, 2 H), 6.90 (s, 2 H), 4.34 (s, 2 H), 2.29 (s, 3 H), 2.19 (s, 6 H).

1-(4-Acetylphenyl)-2-phenylethanone (15c)

1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.6 Hz, 2 H), 8.00 (d, J = 8.6 Hz, 2 H), 7.36-7.20 (m, 5 H), 4.30 (s, 2 H), 2.62 (s, 3 H).

4-(Phenylacetyl)benzaldehyde (16c)

1H NMR (300 MHz, $CDCl_3$): δ = 10.08 (s, 1 H), 8.13 (d, J = 8.3 Hz, 2 H), 7.95 (d, J = 8.3 Hz, 2 H), 7.35-7.15 (m, 5 H), 4.31 (s, 2 H).

2-Phenyl-1-(4-trifluoromethylphenyl)ethanone (17c)

1H NMR (300 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 8.0 Hz, 2 H), 7.35-7.15 (m, 5 H), 4.30 (s, 2 H).

1-(4-Fluorophenyl)-2-phenylethanone (18c)

1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (dd, J = 7.4 and 5.5 Hz, 2 H), 7.35-7.20 (m, 5 H), 7.11 (t, J = 7.4 Hz, 2 H), 4.25 (s, 2 H).

2-Phenyl-1-*p*-tolyl-ethanone (19c)

1H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 2 H), 7.35-7.10 (m, 7 H), 4.25 (s, 2 H), 2.39 (s, 3 H).

1-(4-*tert*-Butylphenyl)-2-phenylethanone (20c)

^1H NMR (300 MHz, CDCl_3): δ = 7.95 (d, J = 8.0 Hz, 2 H), 7.46 (d, J = 8.0 Hz, 2 H), 7.35-7.15 (m, 5 H), 4.25 (s, 2 H), 1.31 (s, 9 H).

1-(4-Methoxyphenyl)-2-phenylethanone (21c)

^1H NMR (300 MHz, CDCl_3): δ = 7.99 (d, J = 8.6 Hz, 2 H), 7.35-7.20 (m, 5 H), 6.91 (d, J = 8.6 Hz, 2 H), 4.22 (s, 2 H), 3.85 (s, 3 H).

1-(6-Methoxynaphthalen-2-yl)-2-phenylethanone (22c)

^1H NMR (300 MHz, CDCl_3): δ = 8.47 (s, 1 H), 8.03 (d, J = 8.6 Hz, 1 H), 7.84 (d, J = 8.2 Hz, 1 H), 7.75 (d, J = 8.2 Hz, 1 H), 7.35-7.10 (m, 7 H), 4.38 (s, 2 H), 3.94 (s, 3 H).

1-Phenyl-2-phenylethanone (23c)

^1H NMR (300 MHz, CDCl_3): δ = 8.00 (d, J = 7.4 Hz, 2 H), 7.65-7.15 (m, 8 H), 4.28 (s, 2 H).

1-Naphthalen-1-yl-2-phenylethanone (24c)

^1H NMR (300 MHz, CDCl_3): δ = 8.55 (d, J = 8.3 Hz, 1 H), 7.95 (m, 2 H), 7.84 (d, J = 8.2 Hz, 1 H), 7.60-7.45 (m, 3 H), 7.35-7.20 (m, 5 H), 4.37 (s, 2 H).

2-Phenyl-1-*p*-tolylethanone (25c)

^1H NMR (300 MHz, CDCl_3): δ = 7.70 (d, J = 7.8 Hz, 1 H), 7.40-7.15 (m, 8 H), 4.20 (s, 2 H), 2.43 (s, 3 H).

2-Phenyl-1-(2,4,6-trimethylphenyl)ethanone (26c)

^1H NMR (300 MHz, CDCl_3): δ = 7.35-7.15 (m, 5 H), 6.81 (s, 2 H), 3.99 (s, 2 H), 2.27 (s, 3 H), 2.12 (s, 6 H).

3-(4-*tert*-Butylphenyl)-3-oxo-propionic acid methyl ester (44c) (Table 5, Entry 1)

^1H NMR (300 MHz, CDCl_3): δ = 7.87 (d, J = 8.4 Hz, 2 H), 7.48 (d, J = 8.4 Hz, 2 H), 3.98 (s, 2 H), 3.74 (s, 3 H), 1.33 (s, 9 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 191.9, 167.0, 156.5, 133.4, 128.5, 125.8, 52.4, 45.6, 35.2, 31.0.

3-(4-Methoxyphenyl)-3-oxo-propionic acid methyl ester (45c) (Table 5, Entry 2)

^1H NMR (300 MHz, CDCl_3): δ = 7.91 (d, J = 8.8 Hz, 2 H), 6.93 (d, J = 8.0 Hz, 2 H), 3.95 (s, 2 H), 3.86 (s, 3 H), 3.73 (s, 3 H).

3-Methoxy-3-*o*-tolyl-acrylic acid methyl ester (46c)

^1H NMR (300 MHz, CDCl_3): δ = 7.82 (m, 2 H), 7.25 (m, 2 H), 3.97 (s, 2 H), 3.74 (s, 3 H), 2.16 (s, 3 H).