

### 3-Benzoylthiophenes from 3-Thienyl-manganese Bromides

#### Rieke Manganese<sup>1</sup>

A mixture of lithium (20 mmol), naphthalene (2 mmol), and 10 mmol of manganese chloride was added via syringe freshly distilled THF at room temperature, and then the resulting mixture was allowed to stir at room temperature for 1-3 h. A black slurry was obtained and ready for use.

#### Coupling of 3-Thienyl-manganese Bromides with Acid Chloride

To a slurry of Rieke manganese (10.0 mmol) in THF (10 mL) under argon was added 3,4-dibromothiophene (5.0 mmol) at room temperature, and the mixture was stirred at room temperature for 5 h. 1,2-Dibromoethane 21 (6.0 mmol) was added neat to the reaction mixture at 0 °C, and the mixture was allowed to warm to room temperature over 20 min. To the resulting organomanganese reagent was added acid chloride (3.0 mmol) neat at room temperature via syringe. The resulting mixture was stirred at room temperature for 30 min. The mixture was quenched with 3 M HCl (10 mL) and extracted with ether (2 x 10 mL), and the combined organic layers were sequentially washed with saturated NaHCO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaCl solutions, dried over MgSO<sub>4</sub>, and concentrated. Flash chromatography (ethyl acetate/ hexanes) afforded the corresponding ketones in 34-91% isolated yield.

#### 3- Bromo- 4-( 4- bromobenzoyl) thiophene<sup>2</sup>:

Yield 62 %.

<sup>1</sup> H NMR  $\delta$  7.72-7.59 (m, 5H), 7.39 (d, J = 3.57 Hz, 1H).

<sup>13</sup> C NMR  $\delta$  188.67, 138.79, 136.09, 132.33, 132.29, 131.75, 131.40, 128.46, 125.30, 110.35.

EIMS m/z (relative intensity) 348.80 (33), 345.80 (M + , 14), 344.80 (43), 190.85 (99), 188.85 (100), 184.80 (41).

#### Ethyl 4-(3-bromo-4-thienyl) benzoate<sup>2</sup>:

Yield 86 %.

<sup>1</sup> H NMR  $\delta$  8.10 (dd, J ) 8.59, 5.00 Hz, 2H), 7.58 (dd, J = 8.50, 5.00 Hz, 2H), 7.40 (d, J = 3.50 Hz, 1H), 7.33 (d, J = 4.00 Hz, 1H), 4.40 (q, J = 7.50 Hz, 2H), 1.41 (t, J = 7.00 Hz, 3H).

<sup>13</sup> C NMR  $\delta$  167.03, 140.17, 130.14, 129.60, 125.23, 124.96, 111.37, 61.70, 15.00.

HRMS calcd for C<sub>13</sub>H<sub>11</sub>BrO<sub>2</sub>S 310.0770, found 309.9663.

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<sup>1</sup> TL 1997 993  
<sup>2</sup> JOC 1997 6921