Copper Nitrate-Catalyzed *alpha*-Bromination of Aryl Ketones with Hydrobromic Acid

Jianqiang Wang, Xiaolei Wang, Zong-Qiang Niu, Jian Wang, Man Zhang and Jing-Hua Li*
College of Pharmaceutical Sciences, Zhejiang University of Technology, 310032, Hangzhou, China
E-mail: lijh@zjut.edu.cn.

Supporting Information

Content

1. Analytical data for 2a~2r	1-4
2. Analytical data for the bromination product of acetone	5
3. References	5-6
4. ¹ H NMR spectra for 2a~2r	6-15
5. ¹ H NMR spectrum for the bromination product of acetone	16

1. Analytical data for 2a~2r

2-Bromo-1-phenylethanone ^[1] (2a)

Solid, mp: 47–48 °C (lit. ^[2], 49–50 °C), ¹H NMR (500 MHz, CDCl₃): δ 4.48 (s, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 7 Hz, 2H).

2-Bromo-1-p-tolyethanone (2b)

Solid, mp: 48–49 °C (lit. ^[2,3], 48–50 °C), ¹H NMR (500 MHz, CDCl₃): δ 2.44 (s, 3H), 4.44 (s, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H).

2-Bromo-2,3-dihydro-1H-inden-1-one (2c)

Solid, mp: 37–38 °C (lit.^[4], 37–38 °C), ¹H NMR (500MHz, CDCl₃): δ 3.44 (dd, J = 18 Hz and 3 Hz, 1H), 3.85 (dd, J = 18 Hz and 7.5 Hz, 1H), 4.67 (dd, J = 7.5 Hz and 3 Hz, 1H), 7.44–7.48 (m, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H).

2-Bromo-3,4-dihydronaphthalen-1(2H)-one^[5] (2d)

Yellow oil, ¹H NMR (500 MHz, CDCl₃): δ 2.45–2.56 (m, 2H), 2.95 (dt, J = 17.0 Hz and 4.5 Hz, 1H), 3.30–3.37 (m, 1H), 4.75 (t, J = 4.5 Hz, 1H), 7.28–7.31 (m, 1H), 7.35–7.38 (m, 1H), 7.52–7.56 (m, 1H), 8.10–8.12 (m, 1H).

2-Bromo-1-(4-chlorophenyl)ethanone^[1] (2e)

Solid, mp: 95–96 °C (lit.^[2] 96–97 °C), ¹H NMR (500 MHz, CDCl₃): δ 4.42 (s, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H).

2-Bromo-1-(2-chlorophenyl)ethanone^[7] (2f)

Oil, ¹H NMR (500 MHz, CDCl₃): δ 4.54 (s, 2H), 7.36–7.39 (m, 1H), 7.39–7.41 (m, 2H), 7.57–7.59 (m, 1H).

2-Bromo-1-(4-fluorophenyl)ethanone (2g)

Solid, mp: 48–49 °C (lit.^[8] 49–50 °C), ¹H NMR (500 MHz, CDCl₃): δ 4.43 (s, 2H), 7.17–7.20 (m, 2H), 8.03–8.06 (m, 2H).

2-Bromo-1-(4-nitrophenyl)ethanone^[1] (2h)

Solid, mp: 96–97 °C (lit.^[2] 96–96.5 °C), ¹H NMR (500 MHz, CDCl₃): δ 4.48 (s, 2H), 8.18 (d, *J* = 9.0 Hz, 2H), 8.36 (d, *J* = 9.0 Hz, 2H).

2-Bromo-1-phenylpropan-1-one^[1] (2i)

Solourless oil, ¹H NMR (500 MHz, CDCl₃): δ 1.92 (d, *J* = 6.5 Hz, 3H), 5.31 (q, *J* = 6.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 8.03-8.05 (m, 2H).

2-Bromo-2-methyl-1-phenylpropan-1-one^[1] (2j)

colourless oil, ¹H NMR (500 MHz, CDCl₃): δ 2.05 (s, 6H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 1.0 Hz, 1H), 8.16 (d, *J* = 1.0 Hz, 1H).

2-Bromo-1-phenylbutane-1,3-dione^[9] (2k)

Solid, mp: 40-41 °C (lit.,^[6] 43-45 °C), ¹H NMR (500 MHz, CDCl₃): δ 2.48 (s, 3H), 5.63 (s, 1H), 7.51–7.53 (m, 2H), 7.64–7.66 (m, 1H), 7.99–8.01 (m, 2H).

Ethyl 2-bromo-3-oxo-3-phenylpropanoate^[9] (2l)

Colourless oil, ¹H NMR(500 MHz, CDCl₃): δ 1.26 (t, *J* = 7 Hz, 3H), 4.30 (q, *J* = 7 Hz, 2H), 5.68 (s, 1H), 7.50–7.53 (m, 2H), 7.63–7.65 (m, 1H), 8.00–8.02 (m, 2H).

2-Bromo-2-phenylacetophenone^[1] (2m)

Solid, mp: 53–54 °C (lit.,^[10] 54-55 °C), ¹H NMR (500 MHz, CDCl₃): δ 6.40 (s, 1H), 7.35–7.41 (m, 3H), 7.45–7.48

(m, 2H), 7.55–7.60 (m, 3H), 8.00–8.02 (m, 2H).

2-Bromo-1-(4-fluorophenyl)-2-phenylethanone ^[11] (**2n**)

Oil, ¹H NMR (500 MHz, CDCl₃): δ 6.35 (s, 1H), 7.11–7.15 (m, 2H), 7.34–7.41 (m, 3H), 7.53–7.55 (m, 2H), 8.03–8.06 (m, 2H).

2-Bromo-1-(4-chlorophenyl)-2-phenylethanone ^[12] (**2o**)

Solid, mp: 66–67 °C (lit., ^[13] 67.5–68.5 °C), ¹H NMR (500 MHz, CDCl₃): δ 6.30 (s, 1H), 7.32–7.39 (m, 3H), 7.41–7.43 (m, 2H), 7.51 (d, J = 7 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H).

2-Bromo-2-phenyl-1-p-tolyethanone (**2p**)

Solid, mp: 86–87 °C (lit., ^[14] 86–87 °C), ¹H NMR (500 MHz, CDCl₃): δ 2.38 (s, 3H), 6.37 (s, 1H), 7.22–7.24 (m, 2H), 7.29–7.36 (m, 3H), 7.52 (d, J = 8.5 Hz, 2H), 7.88–7.89 (m, 2H).

2-Bromo-2-(4-chlorophenyl)-1-p-tolyethanone ^[15] (**2q**)

Solid, mp: 94–95 °C, ¹H NMR (500 MHz, CDCl₃): δ 2.40 (s, 3H), 6.30 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H).

2-Bromo-2-(4-chlorophenyl)-1-phenylethanone ^[16] (**2r**)

Solid, mp: 62–63 °C, ¹H NMR (500 MHz, CDCl₃): δ 6.33 (s, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.44–7.48 (m, 4H), 7.57 (t, J = 7.5 Hz, 1H), 7.98 (d, J = 7.5 Hz, 2H).

2. Analytical data for the bromination product of acetone^{[17][18][19]}

In the spectra (please refer to 5. ¹H NMR spectrum for the bromination product of acetone) we can find that the bromination product is a mixture of 1-bromoacetone^[17], 1,3-dibromoacetone^[18] and 1,1-dibromoacetone^[19]. Their ¹H NMR (500 MHz, CDCl₃) spectra are: δ 2.35 (s, 3H), 3.89 (s, 2H); δ 4.15 (s, 2H); δ 2.54 (s, 3H), 5.78 (s, 1H), respectively.

1-bromoacetone:

1,3-dibromoacetone:

1,1-dibromoacetone

3. References

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4. ¹H NMR spectra for 2a~2r

5. ^1H NMR spectrum for the bromination product of acetone