Highly efficient method for Synthesis of benzoquinones using Hypervalent iodine (III) reagent and sodium bisulfate

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Supporting Information:

GENERAL PROCEDURE

General procedure for synthesis of benzoquinone derivatives (Table 3, entry 1): (Diacetoxyiodo) benzene (5 mmol, 1.61g) and NaHSO₄.H₂O (1mmol, 0.138g) were stirred for 10-15 min, at room temperature in aqueous solution of acetonitrile (5 ml water and 5 ml acetonitrile). In this reaction mixture benzamide (1mmol) was added and stirring was continuing till reaction goes to completion (TLC). After completion of reaction, the reaction mixture was quenched with water and further extracted with chloroform (3×10 ml). The combined chloroform layers were washed with water (3×20ml) dried over Na₂SO₄, and concentrated on rota-evaporator to get the crude residue. The residue was further purified by column chromatography on silica gel using ethyl acetate: hexane (1:9) as an eluent to afford pure benzoquinone.

Characterization Data of benzoquinone derivatives:

1, 4-Benzoquinone (Table 2, Entry 1)¹:

Mp 115 °C (Lit ^[1] Mp 112 °C); ¹H NMR (60 MHz, CDCl₃): 7.59-7.68 (s, 4H); IR (KBr): 3165, 3070, 1665, 1589, 1312, 1264, 897

2-Methyl-1, 4-benzoquinone (Table 2, Entry 2)²:

Mp 68-69 °C (Lit ^[2] Mp 69 °C); IR (KBr): 3728, 3021, 2317, 1656, 1604, 1452, 1218, 904, 757. ¹H NMR 60 MHz (CDCl₃): δ 2.04 (s, 3H), 6.56 (s, 1H), 6.65-6.70 (m, 2H).

2-Chloro-1, 4-benzoquinone (Table 2, Entry 3)³:

Mp 54-56 °C (Lit ^[3] Mp 55-56 °C); ¹H NMR 60 MHz (CDCl₃): δ 6.80 (d, 1H), 7.3 (d, 1H), 6.73 (s, 1H).

1, 4-benzoquinone (Table 2, Entry 4)⁴:

Mp 114-116 °C (Lit ^[4] Mp 115 °C); ¹H NMR 300 MHz (CDCl₃): δ 3.81 (s, 3H), 5.93 (br s, 1H), 6.71 (br s, 2H).

1, 4 benzoquinone (Table 2, Entry 5)⁵:

Mp 115 °C (Lit ^[5] Mp 115 °C); ¹H NMR (60 MHz, CDCl₃): 7.59-7.68 (s, 4H); IR (KBr): 3165, 3070, 1665, 1589, 1312, 1264, 897

1, 4 benzoquinone (Table 2, Entry 7)⁶:

Mp 115 °C (Lit ^[6] Mp 111 °C); ¹H NMR (60 MHz, CDCl₃): 7.58-7.68 (s, 4H); IR (KBr): 3165, 3070, 1665, 1589, 1312, 1263, 897

4-Hydroxy-2, 4, 6-trimethylcyclohexa-2, 5-dienone (Table 2, Entry 8)⁷:

Mp 45-46 °C (Lit ^[7] Mp 45-46 °C); ¹H NMR 300 MHz (CDCl₃): δ 1.41 (s, 3H), 1.84 (s, 6H), 6.62 (br s, 2H); ¹³C NMR δ 187.0, 147.9, 132.9, 66.8, 26.9, 15.7

2-Methoxy-1, 4-benzoquinone (Table 2, Entry 9)⁸:

Mp 142-144 °C (Lit ^[8] Mp 142 °C); ¹H NMR 300 MHz (CDCl₃): δ 3.81 (s, 3H), 5.93 (br s, 1H), 6.71 (br s, 2H)

4-Hydroxy-4-methylcyclohexa-2, 5-dienone (Table 2, Entry 10)⁹:

Mp 77-78 °C (Lit ^[9] Mp 74 °C); IR (KBr) 3411, 2974, 2921, 1674, 1644, 1372 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 1.46 (s, 3 H), 2.02 (s, 1 H), 6.12 (d, 2 H), 6.88 (d, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.1 (q), 17.0 (t), 42.0 (t), 70 (s), 128.2 (d), 151.4 (d), 185.7 (s)

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