

Oxidative transformation of alcohols and organic halides in aqueous solution

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Supplementary Information (New J Chem. 2014)

1. Preparation of quinolinium chlorochromate: Quinoline (0.11 mol, 13 mL) was added dropwise to an ice cooled and continuously stirred mixture of chromium trioxide (0.1 mol, 10 g) and conc. HCl (11 mL) in distilled water (10 mL). The yellow orange solid was collected on a sintered funnel and dried in vacuum (22.4 g, 77%).

IR (Neat, cm^{-1}): 3200, 2986, 1636, 1594, 1554, 610, 473.

^1H NMR (dDMSO, 400 MHz) δ : 9.33 (s, 1H, NH), 9.13 (d, 1H, ArH, $J=4.2$), 8.34-8.26 (m, 3H, ArH), 8.12-7.93 (m, 2H, ArH), 7.73 (s, 1H, ArH).

^{13}C NMR (dDMSO, 400 MHz): 146.13, 144.27, 139.72, 133.41, 128.87, 128.33, 122.49, 121.71.

2. Oxidation of alcohols and halides:

a) Benzaldehyde:

i) From benzyl alcohol: QCC (7.5 mmol, 2.02 g) was added to benzyl alcohol (5 mmol, 0.50 mL) in distilled water (15 mL) and stirred at room temperature for 4 h. The progress of the reaction was monitored by TLC and the product was extracted using diethyl ether (3×5mL). The organic ether layer was washed with dil. HCl solution (5 mL), distilled water (2×5 mL) and finally dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure followed by the purification of the 40 mg of the crude product using preparative TLC afforded benzaldehyde (24.7 mg, 62%).

ii) From benzyl chloride: Sodium hydroxide (10 mmol, 0.40 g) was dissolved in water (15 mL) followed by the addition of benzyl chloride (5 mmol, 0.50 mL) at a temperature between 45-50°C and stirred for 2.5 h. Contents were cooled to room temperature followed by the addition of QCC (5 mmol, 2.02g). The reaction mixture was further stirred for 5.5 h and the progress of the reaction was monitored by TLC, followed by the usual work up to afford benzaldehyde (15.1 mg, 38%).

IR (Neat, cm^{-1}): 3064, 2819, 2737, 1701, 1597, 746, 688.

^1H NMR (CDCl_3 , 400 MHz) δ : 9.96 (s, 1H, CHO), 7.84-7.44 (m, 5H, ArH).

3. Preparation of 1-(1-Bromopropan-2-yl)-2-(2, 4-dinitrophenyl) hydrazine (2):

2,4-dinitrophenyl hydrazine (**1**, 10 mmol, 1.98 g) was added to ethanol (6 mL) followed by the addition of 1-bromopropan-2-one (10 mmol, 1.36 mL) and acetic acid (two drops) at room temperature. Contents were stirred for 5 h and the solid obtained was filtered to get the crude product that was washed with dil. HCl (5 mL) and water (2 X 5 mL); and finally recrystallized in ethanol to give 1-(1-bromopropan-2-yl)-2-(2,4-dinitrophenyl) hydrazine (2.1 g, 66%).

IR (Neat, cm^{-1}): 3108, 2925, 1622, 1506, 1428, 1335, 925.

^1H NMR (CDCl_3 , 400 MHz) δ : 10.96 (s, 1H, NH), 9.0 (d, 1H, ArH, $J=2.6$), 8.44(dd, 1H, ArH, $J_1=8.8$, $J_2=2.6$), 7.87 (d, 1H, ArH, $J=8.8$), 4.24 (s, 2H, CH_2Br), 2.11 (s, 3H, CH_3).

^{13}C NMR (CDCl_3 , 400 MHz): 156.1, 146.2, 140.1, 134.3, 130.5, 118.5, 114.6, 36.7, 9.1.

4. Preparation of 2-(bromomethyl)-5,7-dinitro-1H-indole (3):

1-(1-Bromopropan-2-yl)-2-(2,4-dinitrophenyl) hydrazine (3.5 mmol, 1.10 g) was mixed with polyphosphoric acid (3 mmol, 1.01 g) at room temperature and the mixture was heated on a sand bath at 115-125°C for 30 min. Reaction mixture was cooled to 50°C followed by the addition of distilled water (20 mL) to get the crude solid that was filtered and washed with cold water (10 mL) followed by ethanol (10 mL). Finally, recrystallization in ethanol afforded pure 2-(bromomethyl)-5,7-dinitro-1H-indole (0.87 g, 83%).

IR (Neat, cm^{-1}): 3106, 2920, 1618, 1536, 1517, 1424, 1338, 1137, 916.

^1H NMR (CDCl_3 , 400 MHz) δ : 11.08 (s, 1H, NH), 9.10 (d, 1H, ArH, $J=2.6$), 8.41 (dd, 1H, ArH, $J_1=8.8$, $J_2=2.6$), 7.83 (d, 1H, ArH, $J=8.8$), 4.21 (s, 2H, CH_2Br).

^{13}C NMR (CDCl_3 , 400 MHz): 144.7, 138.6, 137.5, 130.1, 129.9, 121.1, 116.7, 116.3, 35.69.

Mass (m/z): 298.9, 300.8.

5. Oxidation of 2-(bromomethyl)-5,7-dinitro-1H-indole (3) to 5,7-dinitro-1H-indole-2-carbaldehyde (4):

Sodium hydroxide (2 mmol, 0.08 g) was dissolved in distilled water (3 mL) followed by the addition of 2-(bromomethyl)-5,7-dinitro-1H-indole (1 mmol, 0.30 g) and the temperature was raised to 45-50°C. The mixture was stirred for 2.5 h at same temperature and then cooled to room temperature followed by the addition of QCC (1.5 mmol, 0.45g) which was further stirred for 5.5 h. After the completion of reaction the product was extracted using diethyl ether (3×5mL)

and the combined organic layer was washed with dil. HCl solution (5mL), distilled water (2×5 mL) and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure afforded crude product, which upon purification by preparative TLC afforded 5,7-dinitro-1H-indole-2-carbaldehyde (32.54 mg, 33%).

IR (Neat, cm⁻¹): 3106, 2924, 2855, 1721, 1618, 1520, 1501, 1425, 1331.

¹H NMR (CDCl₃, 400 MHz) δ: 11.01 (s, 1H, NH), 9.60 (s, 1H, CHO), 9.10 (d, 1H, ArH, J= 2.7), 8.46 (dd, 1H, ArH, J₁= 9.2, J₂= 2.7), 7.34 (d, 1H, ArH, J= 9.2).

¹³C NMR (CDCl₃, 400 MHz): 182.2, 146.2, 144.6, 138.5, 132.5, 131.8, 121.7, 116.8, 116.4.

Mass (m/z): 238.1.

6. Removal of chromium (VI):

The removal of chromium (VI) from the aqueous waste was performed in the following steps:

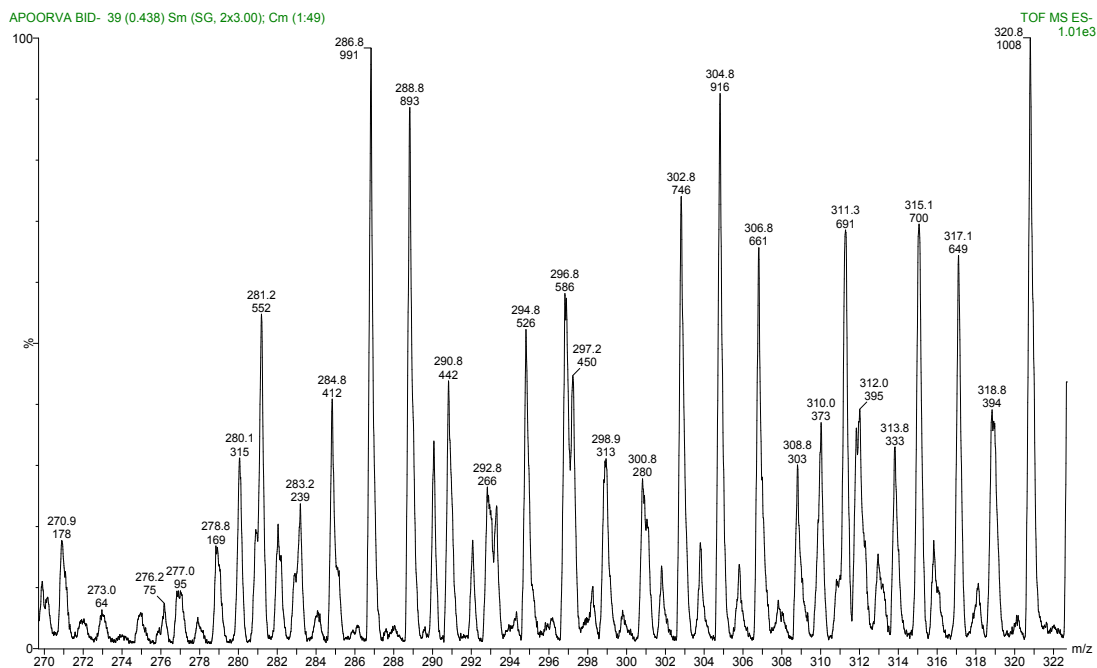
Collection of the aqueous waste: QCC (22.5 mmol, 6.07g) was added to distilled water (45 mL) followed by the addition of benzyl alcohol (15 mmol, 1.5 mL). Reaction mixture was stirred at room temperature for 3.5 h and the product was extracted using diethyl ether (3×10 mL). The aqueous waste was filtered to remove the solid mass containing chromium. Solid residue was dried at 50°C and its weight was 3.65 g, which corresponds to 60% of the weight of QCC added to reaction mass before the start of the reaction. The pH of the filtrate was also noted and was found to be 3.

Removal of Cr⁶⁺ by chemical precipitation: Filtrate (27 mL) containing the unconsumed Cr⁶⁺ [along with traces of Cr⁴⁺] has been reduced to Cr³⁺ by using ferrous sulphate as the reducing agent and calcium hydroxide as the coagulant. Ferrous sulphate (15 mmol, 4.17 g) and calcium hydroxide (5 mmol, 0.37 g) were added to the filtrate and the mixture was stirred for 2 h, followed by its filtration. The filtrate obtained at this stage was colourless and its pH was found to be 3.97. The titration of the reduced filtrate was carried out but end point could not be detected indicating absence of the Cr⁶⁺ in it. Acidic filtrate having pH 3.97 was made neutral by adding 15.2 mL of 0.1N calcium hydroxide solution and safely discarded.

pH before reduction = 3.0

pH after reduction = 3.9

7. Mass Spectrum of 2-(bromomethyl)-5,7-dinitro-1H-indole (3):



8. Mass Spectrum of 5,7-dinitro-1H-indole-2-carbaldehyde (4):

