An improved procedure for the synthesis of 2-hydroxybenzaldehyde and 2-hydroxynaphthalene-1-carbaldehyde

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An easy and convenient method is reported for the synthesis of 2-hydroxybenzaldehyde and 2-hydroxynaphthalene-1-carbaldehyde from corresponding phenols by Reimer–Tiemann reaction using aqueous ethyl alcohol and avoiding steam/vaccum distillation.

Keywords: phenol, 2-hydroxybenzaldehyde, 2-napthol, 2-hydroxynaphthalene-1-carbaldehyde

2-Hydroxybenzaldehyde and 2-hydroxynaphthalene-1-carbaldehyde are widely used in the organic and pharmaceutical industry. The present literature method[1,2] for the preparation of 2-hydroxybenzaldehyde by the Reimer–Tiemann reaction is refluxing phenol and sodium hydroxide dissolved in water and chloroform at 60–70 °C for 1.45 h. Unreacted chloroform is removed by steam distillation. Then the reaction mixture is acidified by dil. HCl and further steam distilled to obtain 2-hydroxybenzaldehyde in 35% yield. This procedure requires steam distillation twice. In the preparation of 2-hydroxy-naphthalene-1-carbaldehyde steam as well as vaccum distillation is needed. Cochran *et al.*[3] studied the Reimer–Tiemann reaction under ultrasound conditions and other approaches have been applied by Thoer *et al.*[4] and Narasimhan *et al.*[5] These methods are time and energy consuming, and the yield of product is still low.

We report here a simple and convenient procedure, which is inexpensive and the yield of ortho-isomer is more than the conventional method. No further purification is required and time as well as energy is saved due to avoiding steam/vaccum distillation.

The literature method[6-8] for the preparation of 2-hydroxy-naphthalene-1-carbaldehyde requires vaccum distillation for purification of the aldehyde. We report here a synthesis where vaccum distillation is not necessary. The best yields of 2-hydroxynaphthalene-1-carbaldehyde were obtained with 40% aqueous ethyl alcohol.

A typical procedure

2-hydroxybenzaldehyde

Phenol [0.1 mol, 9.6 g] and sodium hydroxide [30.7 g in 27.7 ml water and 3.0 ml ethyl alcohol] were heated to 65 °C while chloroform [0.19 mol, 15 ml] was added over 45 min to maintain refluxing. It was then heated a further 1 h at 65–70 °C and then cooled to 20–25 °C for 3 h. The solid that separates out was filtered off and washed with ethyl alcohol. Solid was dissolved in the minimum amount of water and then acidified with dil. HCl. The liquid product separates out and was extracted with ether. On evaporating the ether 2-hydroxybenzaldehyde separates out. Yield 45%, b.p. 197 °C (literature b.p.197 °C) m.p. of 2,4-dinitrophenylhydrazone: 252 °C (literature m.p. 252 °C).

2-hydroxynaphthalene-1-carbaldehyde

2-Napthol (0.1 mol, 14.4 g), sodium hydroxide (46 g) dissolved in 23 ml water and 23 ml ethyl alcohol was heated to 70–75 °C. Chloroform (0.15 mol, 13 ml) was added over 45 min to mantain reflux. The mixture was heated at 75–80 °C for a further 1 h. and then cooled to 20–25 °C for 3 h. The solid that separates out was filtered off and washed with ethyl alcohol. It was dissolved in the minimum amount of water then acidified with dil. HCl. The solid which separates out was washed with water and recrystallised from ethyl alcohol. Yield 65%, m.p. 81 °C. (literature m.p. 80 °C) m.p. of 2,4-dinitro-phenylhydrazone: 260 °C

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