Cannizzaro reaction (Benzaldehyde reduction-oxidation)

Add into a wide neck 250 ml Erlenmeyer flask potassium hydroxide solution (a cooled solution of 14.5 g KOH and 14 ml water)\(^1\) and benzaldehyde\(^2\) (16 g; 0.15 mol; 15 ml). After the addition shake the sealed flask (do not use ground neck flasks) intensively until a strong emulsion is forming (20-25 min). Let this emulsion stay in the closed flask at room temperature until the next lab practice\(^3\).

At the next lab add sufficient amount of water to dissolve the forming potassium benzoate,\(^4\) then pour the forming slurry to a separatory funnel\(^5\) and extract it with dichloromethane (3×15 ml). Store the aqueous phase and wash the unified dichloromethane layers with saturated sodium metabisulfite solution\(^6\) (2×10 ml), 10% sodium bicarbonate solution (10 ml) and water (10 ml). After drying\(^7\) remove the dichloromethane in vacuum rotary evaporator and purify the residual oil by distillation in vacuum. Usual yield is 6.5 g (86 %) of benzyl alcohol.

Pour the extracted (and stored) aqueous layer into ice-cooled acid (50 g of ice, 40 ml of water and 40 ml of conc. hydrochloric acid). Collect the precipitating benzoic acid by filtration, wash it with a few amount of cold water and recrystallize it from water (ca. 15 ml/g crude product). The recrystallized product is white crystalline solid (6.6 g; 78 %; m.p 121 °C).

Notes

(1) Add the solid KOH in small portions to stirred and cooled water. The potassium hydroxide solution can be substituted by a solution of sodium hydroxide (16 g) in water (13 ml).

(2) The benzaldehyde should be free from benzoic acid.

(3) The minimum required reaction time at room temperature is 24 h.

(4) Usually, 50-55 ml of water is sufficient to dissolve the solid. However, the solution process is not immediate. To dissolve the solid effectively, the bigger clumps should be crashed by appropriate devices.

(5) After the transfer, washing the flask with a few amount of water and dichloromethane can reduce the loss of products.

(6) Washing with sodium metabisulfite solution removes the residual benzaldehyde.

(7) Drying should be made over anhydrous potassium carbonate or sodium sulfate. Use of CaCl\(_2\) should be avoided due to its complex forming ability with alcohols.