12.7 Benzoic acid

Apparatus and reagents

Apparatus for reflux (11.4a)
Apparatus for recrystallization (11.6)
Apparatus for melting point (11.7)
Beaker, 100 cm^3
Methylbenzene, 2 cm^3
Potassium manganate(VII), 2 g
Sodium disulphate(IV), solid
Sodium carbonate, solid
Sulphuric acid, 2 M

Procedure

Place 2 cm^3 methylbenzene, 2 g potassium manganate(VII), 20 cm^3 water, and one spatula measure of sodium carbonate in the flask. Set up the apparatus for reflux (11.4a). Reflux the mixture gently until the purple colour disappears. This may take about 2 hours.
Cool the mixture and acidify with dilute sulphuric acid. Add sodium disulphate(IV) to remove the brown residue of manganese(IV) oxide. Filter off the crystals of benzoic acid.
Recrystallize the benzoic acid from hot water (11.6) and check the melting point (11.7), which is 122°C.

12.8 Nitrobenzene

Apparatus and reagents

Apparatus for recrystallization (11.6)
Apparatus for melting point (11.7)
Flask, 50 cm^3
Test-tube, 125 × 15 mm
Glass rod
Methyl benzoate, 2 cm^3
Sulphuric acid, concentrated, 5.5 cm^3
Nitric acid, concentrated, 1.5 cm^3
Methanol, 10 cm^3
Ice

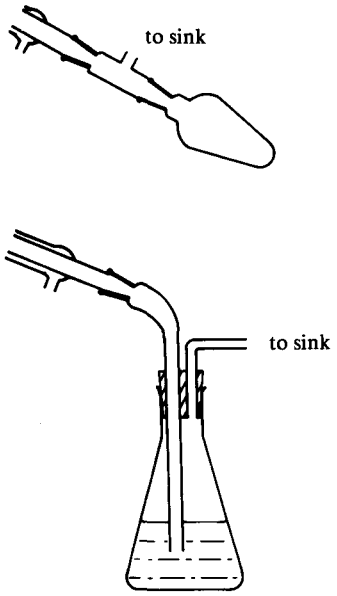
Procedure

Place 4 cm^3 concentrated sulphuric acid and 2 cm^3 methyl benzoate in the flask and cool in ice. Mix together 1.5 cm^3 concentrated nitric acid and 1.5 cm^3 concentrated sulphuric acid in a test-tube. Cool this solution and add dropwise to the solution of methylbenzoate with stirring. This should take about 15 minutes.
Allow the reaction mixture to stand at room temperature for about 15 minutes and then pour onto 20 g of ice. Stir until the product becomes crystalline.
Filter off the product (methyl-3-nitrobenzoate) and wash with 5 cm^3 of methanol. Recrystallize from 5 cm^3 methanol (11.6) and check the melting point (11.7) which is 77-78°C.

12.9 Phenylamine

Apparatus and reagents

Apparatus for reflux with addition (11.4b or 11.4c)
Apparatus for steam distillation (11.3)
Apparatus for solvent extraction (11.1), modified as shown for ethoxyethane distillation
Nitrobenzene, 2 cm^3
Tin, granulated, 5 g
Hydrochloric acid, concentrated, 10 cm^3
Sodium hydroxide, solid, 10 g
Sodium chloride, solid, 5 g
Ethoxyethane
Magnesium sulphate, anhydrous



Procedure

Nitrobenzene vapour is harmful and the first part of the reaction should be carried out in a fume cupboard. Ethoxyethane is highly flammable. Do not use in the room with any source of ignition.
Place 5 g tin (an excess) and 2 cm^3 nitrobenzene in the flask. Set up the apparatus for reflux with addition (11.4b or 11.4c). Add 10 cm^3 concentrated hydrochloric acid slowly: the reaction should not be too violent.
When all the acid has been added and the reaction has subsided, reflux the mixture on a boiling-water bath for 30 minutes. Allow to cool and dissolve any excess tin in a further portion of acid. Meanwhile dissolve 8 g sodium hydroxide in 12 cm^3 water. Dismantle the apparatus and remove the flask to the open laboratory.
Add the sodium hydroxide solution, with shaking until the phenylamine separates as an oil and the tin salts redissolve.
Set up the apparatus for steam distillation (11.3) and steam distil until either about 40 cm^3 of distillate has been collected or no more oily drops of phenylamine can be seen forming.
Dissolve 5 g sodium chloride in the distillate and carry out a solvent extraction with ethoxyethane (11.5). Distil off the ethoxyethane using the apparatus modified as shown. Remove the distillate and replace the receiver. Distil the phenylamine, using an air condenser. Collect the fraction boiling at 180-186°C.