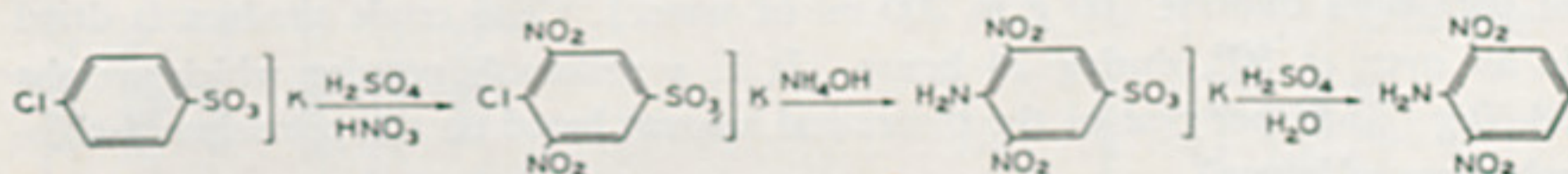


THE PREPARATION OF 2,6-DINITROANILINE

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During the course of our work (1) we needed to prepare 2,6-dinitroaniline. According to the reaction:



we established the procedure here described which is essentially that of Ullmann (2), the final product being obtained by steam distillation. Similar reactions are reported by Holleman and van Haefen (3) and by Welsh (4). 2,6-Dinitroaniline can also be prepared by heating 2,6-dinitroiodobenzene (5), or 2,6-dinitro-phenyl-(4-nitrobenzyl)-ether (6), or 2,6-dinitro-chlorobenzene (7,8) with concentrated alcoholic ammonia; by heating 2,6-dinitroanisole with aqueous ammonia (9); by heating 2,6-dinitro-chlorobenzene or 2,6-dinitrophenol with urea (10); from 2-nitro-phenyl-nitramine and hydrochloric acid in ethereal solution (11); from 2,6-dinitro-dibenzyl-aniline with acetic anhydride and hydrochloric acid (12) and from o-nitroaniline with fuming nitric and sulfuric acid (13).

All details will be given here to facilitate its reproduction:

I. POTASSIUM 3,5-DINITRO-4-CHLOROBENZENESULFONATE (*): In a 1-1 three-necked, round-bottomed flask, fitted with a mechanical stirrer, a thermometer reaching the bottom of the flask and a 200 ml dropping funnel, are placed 50 g (0.21 mole) of crude potassium 4-chloro-benzenesulfonate (**). The flask is cooled in an ice-water bath and, under vigorous stirring,

(*) Lindemann, A. and Wessel, W. describe the simultaneous sulfonation and nitration of chlorobenzene (14).

(**) Potassium 4-chlorobenzenesulfonate can be obtained through the 4-chloro-benzenesulfonylchloride as follows: 105 g (0.5 mole) of crude 4-chloro-benzenesulfonyl chloride is heated in a one liter porcelain dish on the steam bath with a solution of 56 g (1 mole)

200 g (102.5 ml, 2.3 moles) of fuming sulfuric acid (specific gravity 1.95; 23 per cent of sulfur trioxide) are gradually added through the dropping funnel. During this operation the temperature should be maintained under 60°. The stirring is continued and, when the temperature falls to 20°, a mixture of fuming sulfuric and fuming nitric acids (*) is added very slowly through the dropping funnel. A temperature of 25-30° should be maintained during the reaction. After the addition of the sulfuric-nitric mixture, the ice-water bath is removed and the flask is heated on the steam-bath during 5 hours. After cooling, the nitrated compound is added slowly to a filtered solution of 300 g of potassium chloride in 1000 ml of water. Heat is produced with evolution of nitrous vapours. An excessive rise of the temperature must be avoided here and, after cooling, the precipitated potassium 3,5-dinitro-4-chlorobenzenesulfonate is filtered with suction and thoroughly washed with several portions of a solution of potassium chloride (60 g in 200 ml of water). The crude product is dried in an oven at 50°, during 24 hours. It is a yellowish powder which weighs 58-60 g (83-86 per cent of the theoretical amount based on the potassium 4-chlorobenzenesulfonate).

II. POTASSIUM 3,5-DINITRO-4-AMINOBENZENESULFONATE: In a 5 l wide-necked, round-bottomed flask, fitted with a mechanical stirrer, are placed 350 ml of conc. aqueous ammonia (specific gravity 0.9) and, while stirring, 58 g of potassium 3,5-dinitro-4-chlorobenzenesulfonate are added in one portion. The flask is immersed in a cold water-bath, the water being heated *slowly* to prevent excessive foaming. *Caution!* When the water boils, heating and stirring are continued during three hours. After cooling, the product is filtered with suction, without washing and dried in an oven at 50°, during 12 hours. The yield of the dried potassium 3,5-dinitro-4-aminobenzenesulfonate is 46-50 g (84-92 per cent of the theoretical amount).

III. 2,6-DINITROANILINE: The crude potassium 3,5-dinitro-4-aminobenzenesulfonate (48 g) is added to 180-200 ml of 70 per cent sulfuric acid (117 ml of concentrated acid diluted with 78 ml of water) contained in a three-necked, round-bottomed flask of one liter, heated in an oil bath. Through a Pyrex glass tube of 20 mm of internal diameter and about 30 cm in length, this flask is

of potassium hydroxide in 250 ml of water, and the solution almost completely evaporated. The salt, filtered with suction, is repeatedly washed with alcohol and air-dried. The crude material weighs 110-115 g (95.6-100 per cent of the theoretical amount).

4-Chlorobenzenesulfonyl chloride is prepared similarly to 4-acetaminobenzenesulfonyl chloride (15) from 290 g (165 ml, 2.49 moles) of chlorosulfonic acid, freshly distilled and 56 g (50.5 ml, 0.5 mole) of chlorobenzene. The yield of crude material is 100-105 g (95-100 per cent of the theoretical amount based on the chlorobenzene), melting at 37-50°.

(*) The mixture is prepared by carefully adding 70 ml of fuming sulfuric acid (specific gravity 1.95; 23 per cent of sulfur trioxide) to 70 ml of fuming nitric acid (specific gravity 1.5) well cooled in ice-water bath.

connected to a three-necked, round-bottomed flask of five liters, surmounted by two large Allihn-condensers. The crystals of dinitroaniline, formed during the steam-distillation, and which could obstruct the connecting tube are easily removed with the aid of boiling water passing through the opening on top of the tube (see fig. 1).

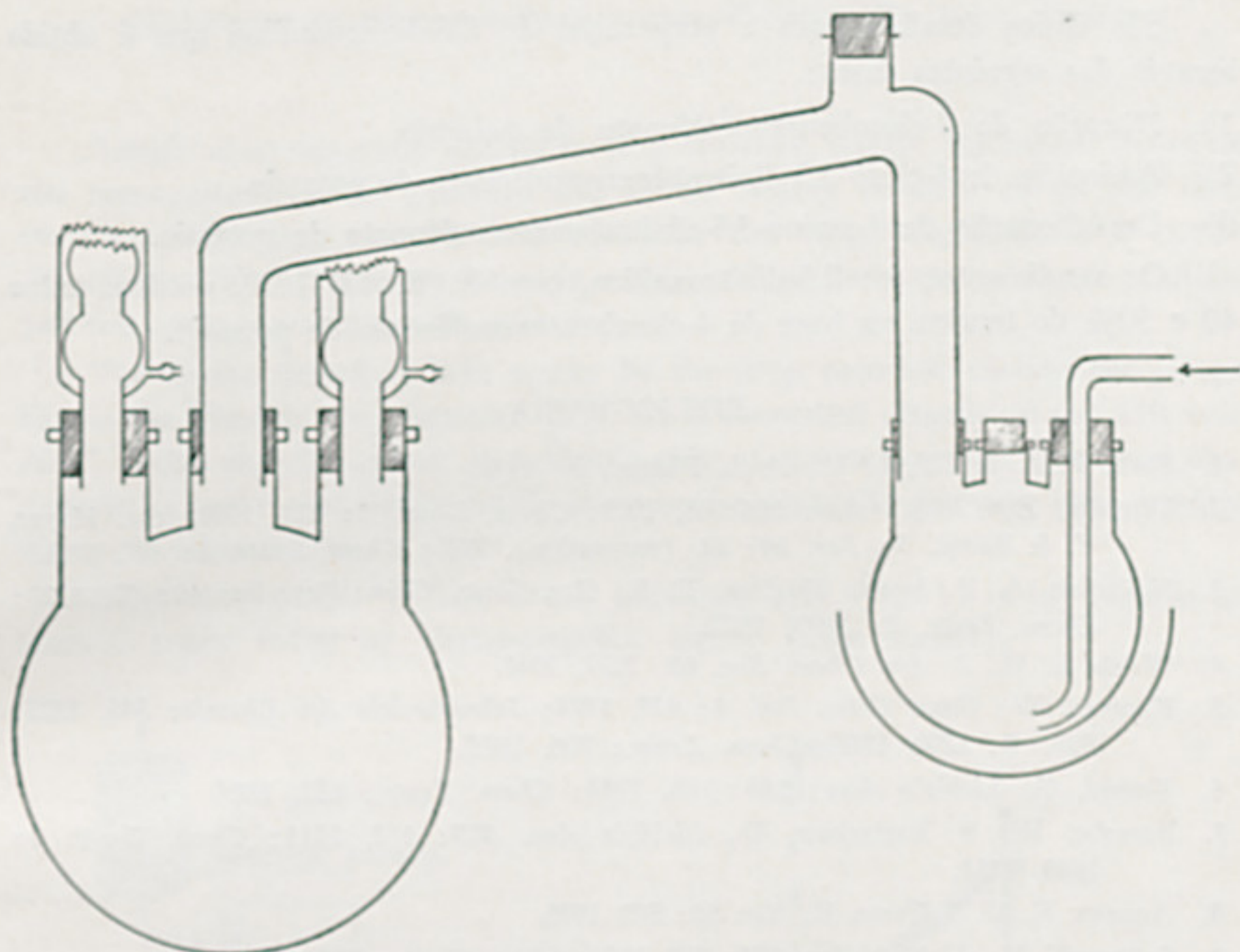


Fig. 1 — Apparatus used for the preparation and steam-distillation of dinitro-aniline. The stoppered hole on the top of the tube which connects the two three-necked flasks is used to remove the crystals which are formed during the distillation and which could block the tube.

When the temperature of the bath reaches 175-180°, steam is passed rapidly through the mixture. The 2,6-dinitroaniline immediately distills and crystallizes in the receiving flask. When 4-5 liters of water are collected all the product has passed. After cooling the distillate in the ice-box, the crystals are filtered by suction and air dried (*). The crude, deep yellow crystals have a melting point of 137-139° and weigh 16-20 g (55-68 per cent of the theoretical amount based on the potassium 3,5-dinitro-4-aminobenzenesulfonate and 40-50 per cent based on the potassium 4-chlorobenzenesulfonate (**). It may be

(*) Extraction of the yellow filtrate with ether is useless.

(**) In the meantime a similar procedure has appeared in *Organic Synthesis* (16); however the final yield there reported (30-36%) is lower than that we obtained in steam-distilled product.

purified by recrystallization from alcohol (20-22 ml/g); after recrystallization the product is obtained as brilliant, deep yellow crystals melting at 138-139.5° (*). The recovery of recrystallization is 70-75%.

RESUMO

São dados detalhes para a preparação de 2,6-dinitroanilina que é obtida através das seguintes fases:

- 1) Nitração de 4-clorobenzenosulfonato de potássio.
- 2) Aminoação de 4-cloro-3,5-dinitrobenzenosulfonato de potássio.
- 3) Dessulfonação de 4-amino-3,5-dinitrobenzenosulfonato de potássio.

Os rendimentos em 2,6-dinitroanilina, com P. F. 137-139°, oscilam entre 40 e 50% do teórico, na base de 4-clorobenzenosulfonato de potássio.

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(*) The melting points recorded in the literature are: 137° (3) 137.8° (5); 138° (9); 138° (12); 138° (11); 138° (10); 138° (13); 138-139° (7); 138.5-139° (4); 141-142° (6).