314. *Preparation of Pure* 1 : 5- *and* 1 : 8-*Dinitronaphthalene and of* 5-*Nitro*-1-*naphthylamine.*

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The separation of the 1 : 5- from the 1 : 8-dinitronaphthalene formed when naphthalene is dinitrated has hitherto been achieved by means of pyridine, sulphuric acid, and acetone (Friedländer, *Ber.*, 1899, **32**, 3531; Eckstein, *Ber.*, 1902, **35**, 3403; Ristenpart, "Organische Farbstoffe," 1911, p. 11). The methods are tedious and in our experiments have failed to give either isomeride pure and in good yield.

It has now been found that (i) boiling aqueous sodium sulphite dissolves only the 1 : 8-dinitronaphthalene, leaving undissolved the whole of the 1 : 5-isomeride; (ii) only the 1 : 5-dinitronaphthalene is reduced, to 5-nitro-1-naphthylamine, by sulphides of sodium, the 1 : 8-isomeride remaining unattacked. Sodium hydrosulphide, disulphide, trisulphide, and pentasulphide give good results, but the monosulphide and ammonium sulphide are less efficient. The addition of magnesium sulphate is beneficial only in reductions with the monosulphide.

Preparation of the Mixture of 1 : 5- *and* 1 : 8-*Dinitronaphthalene.*—The following method is better than those given in Cain's "Manufacture of Intermediate Products for Dyes" (1919,

p. 171). 1-Nitronaphthalene (25 g.) is dissolved in concentrated sulphuric acid (100 c.c.) and nitrated below 5° by the gradual addition of a mixture of 1 part of nitric acid (*d* 1·4) and 5 parts of concentrated sulphuric acid until the solution has turned to a pale straw colour. The colour change is very definite and affords an end-point accurate to within a drop or two of the mixed acid. If a smaller quantity of sulphuric acid is taken, a thick paste is produced which inhibits stirring. The nitration mixture is poured on ice, and the precipitate washed free from acid and left in paste form for interaction with alkaline sulphides, this precaution being essential for efficient working.

Reduction of Pure 1 : 5-*Dinitronaphthalene by Sulphides.*—The dinitronaphthalene (5 g.) was stirred with water (70 c.c.) at 90°, and a solution of the reducing agent (see table below) in water (40 c.c.) at 90° added during 15 minutes; after being maintained for a further 5 minutes at 90°, the mixture was cooled, and the precipitate removed and extracted thrice at 90° with hydrochloric acid (20 c.c. of concentrated acid and 200 c.c. of water). The combined extracts were treated with aqueous ammonia and the precipitate of 5-nitro-1-naphthylamine was removed, dried, and weighed.

Reducing agent.	Mols. used per mol. of 1 : 5-dinitronaphthalene.	% Yield of 5-nitro-1-naphthylamine.
Sodium monosulphide	1·6	29
,, trisulphide...............	1·05	35
,, hydrosulphide	1·6	33
Ammonium sulphide	1·6	18

The residue left after removal of the 5-nitro-1-naphthylamine gave a hydrochloride when its benzene solution was treated with hydrogen chloride, but the base was not identified (Found : N, 12·6%). Variation of the concentration of sodium trisulphide did not alter the yield of 5-nitro-1-naphthylamine obtained.

When pure 1 : 8-dinitronaphthalene was submitted to the procedure described above, each reducing agent produced a black sulphur-containing substance, from which no amine could be extracted. The rates of reaction were much slower at 90° than those for the 1 : 5-isomeride, and were inappreciable below 65°.

Separation of 1 : 8- *from* 1 : 5-*Dinitronaphthalene.*—In each of the following reduction experiments the mixture obtained by the nitration of 1-nitronaphthalene (25 g.) was used.

(a) *Aqueous sodium monosulphide at* 65°. The mixture was stirred with water (200 c.c.) and treated during 15 minutes with a solution of the crystalline monosulphide (17·3 g.) in water (40 c.c.). Stirring was continued for 10 minutes at 65° and for 10 minutes at 90°; then, after cooling, the solid was removed, washed with water, and completely freed from 5-nitro-1-naphthylamine by three extractions with concentrated hydrochloric acid (25 c.c.) and water (350 c.c.) at 90°. The residue was boiled with benzene (250 c.c.) : the hot filtered solution, on cooling, deposited 1 : 8-dinitronaphthalene which, recrystallised from 100 c.c. of benzene, formed very pale yellow, rectangular plates, m. p. 172° (Friedländer, *loc. cit.*, gives m. p. 172°) (Found : N, 13·0. Calc. : N, 12·8%).

(b) *Aqueous sodium trisulphide.* The above procedure was repeated, a solution of sodium monosulphide crystals (11·6 g.) and sulphur (3·1 g.) in water (40 c.c.) being used. The yields recorded are molecular percentages calculated on the quantity of 1-nitronaphthalene nitrated.

Experiment.	% Yield of 5-nitro-1-naphthylamine.	% Yield of 1 : 8-dinitronaphthalene, crude.	purified.
(a)	10·8	35·0 (m. p. 155—168°)	28·6
(b)	9·2	36·2 (m. p. 160—167°)	30·1

(c) *Reductions at* 90°. Although 1 : 8-dinitronaphthalene is converted by aqueous sodium sulphides at 90° into black sulphur-containing substances, in a mixture of the 1 : 5- and the 1 : 8-isomeride the former is attacked first. The reductions were carried out as described above.

Mol. of reducing agent per mol. of 1-nitronaphthalene.	% Yield of crude 5-nitro-1-naphthylamine.	% Yield of crude 1 : 8-dinitronaphthalene (m. p.).
0·5 Sodium monosulphide	11·0	38·5 (160—170°)
0·22 Sodium trisulphide	6·6	48·5 (140—150°)
0·33 ,, ,, ...	12·3	38·1 (166—168°)
0·38 ,, ,, ...	12·85	39·7 (165—168°)
0·44 ,, ,, ...	13·95	35·9 (165—170°)

The black sulphur-containing substance appeared for the first time in the last experiment. When benzene saturated with 1 : 8-dinitronaphthalene was used for the extractions, the yield of crude 1 : 8-dinitronaphthalene increased about 1·2 times; *e.g.*, the 39·7% yield increased to 47%. Estimation by titanous chloride indicated over 99% purity.

(d) *Reductions in presence of magnesium sulphate.*

Mol. of reagent.	Mol. of magnesium sulphate.	Mol. % of 5-nitro-1-naphthylamine.	Mol. % of 1 : 8-dinitronaphthalene (m. p.).
0·5 Sodium monosulphide	0·5	11·7	41·5 (161—167°)
0·33 Sodium trisulphide	1·0	5·5	46·0 (145—155°)
0·33 „ „	0·25	9·2	39·7 (163—167°)

Isolation of Pure 1 : 5-*Dinitronaphthalene.*—When a suspension of the nitration mixture of 1 : 5- and 1 : 8-dinitronaphthalene (1 mol.) in aqueous sodium sulphite (2 mols.) is boiled for 1 hour, the 1 : 8-isomeride dissolves, leaving almost pure 1 : 5-dinitronaphthalene (m. p. 210—215°; yield, 30% of the amount taken) : this crystallises from acetone in colourless needles, m. p. 216° (Found : N, 13·0. Calc. : N, 12·8%).

The authors thank Imperial Chemical Industries, Ltd. (Dyestuffs Group) for various gifts.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, July 29th,* 1933.]