

**432.** *Estimation and Purification of  $\beta$ -Naphthylamine in the Presence of  $\alpha$ -Naphthylamine, and Properties of some Sulphonyl Derivatives.*

By HERBERT H. HODGSON and ERNEST W. SMITH.

THE solubilities of *p*-toluenesulphon- $\alpha$ - and - $\beta$ -naphthalide in 2% aqueous sodium hydroxide at 16° have been found to be 125 g. and 3 g. per litre respectively; the  $\beta$ -naphthalide is practically insoluble in 10% sodium hydroxide solution. In striking contrast, the solubilities of *p*-toluenesulphon- $\alpha$ - and - $\beta$ -naphthalide in 2% aqueous potassium hydroxide are 85 g. and 66 g. per litre respectively. The difference in solubility has been made the basis of a method for estimating  $\beta$ - in the presence of  $\alpha$ -naphthylamine, which depends on the complete precipitation of *p*-toluenesulphon- $\beta$ -naphthalide in the presence of a high concentration of sodium ions. There is a limitation, however: when the concentration of *p*-toluenesulphon- $\alpha$ -naphthalide exceeds 20%, the  $\beta$ -isomeride is only partly precipitated; from the data, it would appear that, for concentrations of the  $\alpha$ -naphthalide between 25% and 56%, the solubility of the  $\beta$ -isomeride is almost exactly proportional to the amount of the  $\alpha$ -naphthalide in solution.

Experiments on the addition of aqueous potassium hydroxide solutions of *p*-toluenesulphon- $\beta$ -naphthalide to solutions containing sodium ions show that sodium can be

detected with ease when the concentration is 2% or higher; the precipitate only forms slowly at a lower concentration, but the crystals are larger and better defined.

When an aqueous acid solution containing both  $\alpha$ - and  $\beta$ -naphthylamine is gradually neutralised, the  $\beta$ -amine is precipitated first; and the hydrochloride of  $\beta$ -naphthylamine separates initially when a benzene solution of both amines is treated with hydrogen chloride. These facts have been utilised for the purification of  $\beta$ -naphthylamine.

The corresponding salts of *m*-nitrobenzenesulphon- $\alpha$ - and - $\beta$ -naphthalide do not exhibit the difference in solubility of their *p*-toluenesulphonyl analogues. They form, however, a remarkable series of hydrates. The *sodium* salts both crystallise with 4 molecules of water; the  $\alpha$ -compound is scarlet; the  $\beta$ -isomeride is cream-coloured, although its aqueous solution is deep reddish-brown. The *potassium* salt of the  $\alpha$ -naphthalide is brick-red, and that of the  $\beta$ -compound is pale yellow; the former is a dihydrate, and the latter a trihydrate. The *barium* salt of *m*-nitrobenzenesulphon- $\beta$ -naphthalide forms a dihydrate. The anhydrous salts all have definite melting points, indicating them to be co-ordinated compounds.

#### EXPERIMENTAL.

*Preparation of p-Toluenesulphon- $\alpha$ - and - $\beta$ -naphthalide.*—Purified  $\alpha$ - or  $\beta$ -naphthylamine (73 g.) was heated with *p*-toluenesulphonyl chloride (150 g.) and water (400 c.c.) for 2 hours on the water-bath with the gradual addition of sodium carbonate so that the liquid was always just alkaline. The naphthalide was then collected, dissolved (the  $\alpha$ -compound in 2% aqueous sodium hydroxide and the  $\beta$ -compound in 2% aqueous potassium hydroxide), and precipitated by carbon dioxide.

*Estimation of  $\beta$ - in Presence of  $\alpha$ -Naphthylamine.*—A mixture of the amines was converted into the mixed *p*-toluenesulphonyl derivatives as described above. These were dissolved by careful heating in 2% aqueous potassium hydroxide (50 c.c. per g. of amine) and the solution was cooled and treated with 20% aqueous sodium hydroxide until precipitation ceased; the sodium salt of the  $\beta$ -naphthalide was removed, and the  $\alpha$ -naphthalide precipitated from the filtrate by carbon dioxide. Alternatively, the sodium salt of the  $\beta$ -naphthalide may be precipitated by powdered anhydrous sodium carbonate, vigorously stirred into the solution. The limitation of the method is indicated by the following data, obtained by using 10% or 20% aqueous sodium hydroxide or anhydrous sodium carbonate as precipitant.

10% Aqueous NaOH.		20% Aqueous NaOH.		Anhydrous Na <sub>2</sub> CO <sub>3</sub> .	
% $\alpha$ in solution.	% $\beta$ precipitated.	% $\alpha$ in solution.	% $\beta$ precipitated.	% $\alpha$ in solution.	% $\beta$ precipitated.
21·0	100·0	25·0	100·0	25·0	100·0
30·0	94·8	30·0	96·6	30·0	100·0
45·0	77·2	40·0	85·5	40·0	90·1
56·0	68·6	50·0	76·8	50·0	81·6
59·7	59·1				
66·6	55·3				

The percentages require a correction of  $\pm 0\cdot2$ .

The *sodium* salt of *p*-toluenesulphon- $\beta$ -naphthalide crystallised from water, containing a trace of sodium hydroxide, in long silky needles, m. p. 370° (Found: S, 10·1. C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>NSNa requires S, 10·0%). On gradual cooling of hot saturated solutions, separation of crystals is sometimes delayed for more than an hour.

The ammonium salt of *p*-toluenesulphon- $\beta$ -naphthalide could not be isolated owing to its facile hydrolysis, since ammoniacal solutions when diluted with water always afforded the original naphthalide.

*Improved Preparation of 2 : 4-Dinitro-1-naphthylamine.*—The method of Morgan and Evens (J., 1919, 115, 1129) has been modified as follows: *p*-toluenesulphon- $\alpha$ -naphthalide (25 g.), dissolved in glacial acetic acid (70 c.c.), was treated with nitric acid (15 c.c.; *d* 1·42) at 50°; the temperature rose to 100°. On cooling, the *p*-toluenesulphon- $\alpha$ -2 : 4-dinitronaphthalide separated in pale yellow needles, m. p. 165° (Morgan and Evens, *loc. cit.*, give m. p. 165—166°); yield, 88%. The naphthalide (22 g.) was heated gradually to 80° with 90% sulphuric acid (66 c.c.); when the clear solution was poured into water (750 c.c.), 2 : 4-dinitro-1-naphthylamine separated in almost quantitative yield; after recrystallisation from glacial acetic acid it had m. p. 242° (Morgan and Evens, *loc. cit.*, give m. p. 239°).

*Precipitation of  $\beta$ - in Presence of  $\alpha$ -Naphthylamine.*—(a) A cold solution of the amines (1 g. of each) in hydrochloric acid (25 c.c.; *d* 1.16) and water (250 c.c.) was gradually neutralised with aqueous sodium hydroxide, the precipitate being collected in three fractions: (1) 0.2 g., m. p. 102°, almost wholly  $\beta$ -amine; (2) 1.0 g., m. p. 92°, mostly  $\beta$ -amine; (3) 0.5 g., m. p. 41°, mainly  $\alpha$ -amine. A method of purifying  $\beta$ -naphthylamine based on these results was carried out as follows: A well-stirred saturated solution of commercial  $\beta$ -naphthylamine (m. p. 102—109°) in dilute hydrochloric acid was gradually precipitated as above until the bulk had separated; m. p. 109—110° (pure  $\beta$ -naphthylamine has m. p. 112°;  $\alpha$ -naphthylamine, m. p. 51°).

(b) A cold solution of  $\alpha$ - and  $\beta$ -naphthylamine (1 g. of each) in benzene was treated with hydrogen chloride. The first precipitate after basification (0.7 g.) had m. p. 102° and was almost pure  $\beta$ -naphthylamine.

*Salts of m-Nitrobenzenesulphon- $\alpha$ - and  $\beta$ -naphthalide.*—The sodium salt of the  $\alpha$ -compound (prepared with J. H. Crook) crystallised from water as a *tetrahydrate* in long, iridescent, scarlet needles, which melted in their water of crystallisation at 85° (Found: H<sub>2</sub>O, 17.0. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SNa, 4H<sub>2</sub>O requires H<sub>2</sub>O, 17.06%). The crystals lost water at 40° and became pale yellow. The loss was continuous up to 50°, chocolate-brown needles of a stable *monohydrate* then being obtained (Found: H<sub>2</sub>O, 4.8. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SNa, H<sub>2</sub>O requires H<sub>2</sub>O, 4.9%). At 120°, the anhydrous salt was obtained in pale orange needles, m. p. 256° (Found: S, 9.2. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SNa requires S, 9.1%). Above 50° the aqueous solution had a deep reddish-brown colour, indicating that the lower hydrate is stable in solution.

The potassium salt of the  $\alpha$ -compound crystallised from water as a *dihydrate* in fine brick-red needles (Found: H<sub>2</sub>O, 8.8. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SK, 2H<sub>2</sub>O requires H<sub>2</sub>O, 8.9%). These lost 2 molecules of water at 120°, leaving the anhydrous salt in pale orange needles, m. p. 232° (Found: S, 8.8. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SK requires S, 8.7%). Solutions of the sodium and potassium salts of *m*-nitrobenzenesulphon- $\alpha$ -naphthalide are readily hydrolysed by aqueous caustic alkali with separation of pure  $\alpha$ -naphthylamine.

*m-Nitrobenzenesulphon- $\beta$ -naphthalide*, prepared similarly to the *p*-toluenesulphonyl analogue above, crystallised from alcohol in pale cream needles, m. p. 166.5° (Found: S, 9.8. C<sub>16</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>S requires S, 9.7%). The sodium salt crystallised from its deep reddish-brown solution in water as a *tetrahydrate* in pale cream micro-needles, m. p. ca. 77° (Found: H<sub>2</sub>O, 17.0. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SNa, 4H<sub>2</sub>O requires H<sub>2</sub>O, 17.06%), which lost 3 molecules of water at 60°, giving pinkish micro-needles of a *monohydrate* (Found: H<sub>2</sub>O, 4.9. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SNa, H<sub>2</sub>O requires H<sub>2</sub>O, 4.9%), and became anhydrous at 120°, forming pale yellow needles, m. p. 290° (Found: S, 9.2. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SNa requires S, 9.1%). The potassium salt crystallised from its deep reddish-brown aqueous solution as a *trihydrate* in pale yellow micro-needles, m. p. ca. 70° (Found: H<sub>2</sub>O, 12.8. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SK, 3H<sub>2</sub>O requires H<sub>2</sub>O, 12.9%), which lost 2 molecules of water at 60°, forming pink-orange micro-needles of a *monohydrate* (Found: H<sub>2</sub>O, 4.5. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SK, H<sub>2</sub>O requires H<sub>2</sub>O, 4.6%), and a further molecule at 120°, giving pale yellow needles of the anhydrous salt, m. p. 240° (Found: S, 8.8. C<sub>16</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>SK requires S, 8.7%). Both the sodium and the potassium salt tend to separate from concentrated solutions as deep red liquids, which may remain fluid for 2—3 days before setting to pale yellow solids. The barium salt crystallised from water in pale orange needles of a *dihydrate* (Found: H<sub>2</sub>O, 4.3. C<sub>32</sub>H<sub>22</sub>O<sub>8</sub>N<sub>4</sub>S<sub>2</sub>Ba, 2H<sub>2</sub>O requires H<sub>2</sub>O, 4.4%), which became anhydrous at 120° as light brown needles; these charred on melting at ca. 280° (Found: N, 7.2. C<sub>32</sub>H<sub>22</sub>O<sub>8</sub>N<sub>4</sub>S<sub>2</sub>Ba requires N, 7.1%).

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