384. *The Preparation of the Ten Dicyanonaphthalenes and the Related Naphthalenedicarboxylic Acids.*

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THE main object of this work was the preparation of derivatives of naphthalene from which substances of the type of phthalocyanine could be prepared and by means of which the structure of phthalocyanine could be confirmed. The dicyanonaphthalenes are also interesting because the acids obtained by their hydrolysis serve (more particularly in the form of their crystalline and low-melting methyl esters) as a set of reference substances for the orientation of dialkylnaphthalenes, which are of importance for the determination of the structure of many natural products. The present work acts as a bridge between these hydrocarbons and the well-known naphthylaminesulphonic acids.

Six dicyanonaphthalenes, the 1 : 2-, 1 : 4-, 1 : 5-, 1 : 6-, 2 : 6-, and 2 : 7-isomerides, were already known when the work was commenced. The usual preparative method had been the cyanide fusion of the salts of the appropriate naphthalenedisulphonic acid or chloronaphthalenesulphonic acid. The reported yields were small and our experiments with 1-chloronaphthalene-2-sulphonic acid and naphthalene-1 : 5-disulphonic acid confirmed that these preparative methods were unsatisfactory. We have prepared all the dicyanonaphthalenes, except the 2 : 3-isomeride, from the alkali salts of the corresponding cyano-sulphonic acids by fusion with alkali ferrocyanide or cyanide.* The yields depended in an interesting manner on the relative positions of the two substituent groups and, where comparison was possible, were much better than those obtainable by the old methods. The cyano-sulphonic acids were prepared by the Sandmeyer reaction from the readily accessible naphthylaminemonosulphonic acids.

The average yields of the nine dicyanonaphthalenes from the pure salts of the cyano-sulphonic acids under standardised conditions are shown in the table. The third line gives the yields obtained by the cyanide fusion of the crude products of the Sandmeyer reaction.

Isomeride *	1 : 2	2 : 1	1 : 3	1 : 4	1 : 5	1 : 6	1 : 7	1 : 8	2 : 6	2 : 7
Yield from purified salt	75	76	17	71	53	18 †	31 ‡	9	42	8%
Yield from crude salt	60	55	9	59	56	10	25	—	29	5%

* The first number denotes the position of the cyano-group.

† The initial material contained inorganic impurity and probably some 1 : 7-isomeride.

‡ The initial material contained inorganic impurity; the yield given is too low.

The reaction appears to be governed by the following rules : (1) There is no difference between the ease of replacement of an α- and a β-sulpho-group by a cyano-group (compare the 1 : 2- and 2 : 1-salts). (2) Reaction is favoured when the sulpho- and the cyano-group are separated by an even number of nuclear carbon atoms (compare the 1 : 2-, 1 : 4-, 1 : 5-, 1 : 7-, and 2 : 6- with the 1 : 3-, 1 : 6-, 1 : 8-, and 2 : 7-salts). (3) When the two groups are separated by an even number of nuclear carbon atoms and are in the same ring, the reaction is independent of the number of carbon atoms (1 : 2-, 2 : 1- and 1 : 4-); but when the groups are in different rings, the yields fall off (1 : 5-, 1 : 7-, 2 : 6-). There appears to be an activation of the sulpho-group by the cyano-group which is transmitted by means of a double bond or conjugated system of double bonds. In the present state of our knowledge of high-temperature reactions of this type it would be premature to define this more exactly.

As 2-naphthylamine-3-sulphonic acid was not accessible, 2 : 3-dicyanonaphthalene was prepared from 2-amino-3-naphthoic acid. The compound $C_{12}H_7O_2N$, m. p. 273°, obtained by treating the diazotised amino-acid with potassium cuprocyanide and subliming the product was shown to be, not 2-cyano-3-naphthoic acid as suggested by Waldmann (*J. pr. Chem.*, 1930, **128**, 150), but the isomeric imide of naphthalene-2 : 3-dicarboxylic acid

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* One reaction of this type has previously been reported : Weissgerber and Kruber obtained 1 : 6-dicyanonaphthalene from potassium 2-cyanonaphthalene-5-sulphonate in 25% yield (*Ber.*, 1919, **52**, 345).

(Freund and Fleischer, *Annalen*, 1913, **402**, 67). The analogous conversion of *o*-cyanobenzoic acid into phthalimide by the action of heat has been observed by Hoogewerf and van Dorp (*Rec. trav. chim.*, 1892, **11**, 91). When 2 : 3-naphthalimide was passed over thoria at 490° in a current of ammonia, it yielded 2 : 3-dicyanonaphthalene (compare Reid and collaborators, *J. Amer. Chem. Soc.*, 1916, **38**, 2128; 1931, **53**, 321).

The melting points of the nitriles and the methyl esters obtained from them in the usual way are tabulated below :

Isomeride	1 : 2	1 : 3	1 : 4	1 : 5	1 : 6	1 : 7	1 : 8	2 : 3	2 : 6	2 : 7
M. p. of dinitrile	190°	179°	208°	263°	211°	167°	232°	251°	293°	267°
M. p. of methyl ester	85°	—	67°	119°	98°	90°	104°	47°	186°	135°

Where comparison is possible, these figures are in substantial agreement with those in the literature. Ruzicka and van Melsen (*Helv. Chim. Acta*, 1931, **14**, 404) gave m. p. 86—87° for the methyl ester of the 1 : 7-acid prepared from 1-methyl-7-ethylnaphthalene (Harvey, Heilbron, and Wilkinson, J., 1930, 423). The figure given above confirms the orientation of this hydrocarbon. Darmstaedter and Wichelhaus (*Annalen*, 1869, **152**, 307) prepared four dicyanonaphthalenes of uncertain orientation. The first, m. p. 204°, was obtained by cyanide fusion of the monosulphonic acid prepared by sulphonating α-bromonaphthalene. Weissgerber and Kruber (*loc. cit.*) have suggested that this is identical with their 1 : 6-dicyanonaphthalene, m. p. 209°, but the 6-sulphonation implied is unacceptable and the present work confirms that this dinitrile and the parent bromosulphonic acid have the 1 : 4-orientation adopted in Beilstein's " Handbuch." From the melting points of the other dinitriles of Darmstaedter and Wichelhaus and on general grounds we think it probable that (1) the acid obtained by the bromination of naphthalene-α-sulphonic acid, which gives a dinitrile, m. p. 236°, is crude 5-bromonaphthalene-1-sulphonic acid; (2) the corresponding bromo-acid from naphthalene-β-sulphonic acid (dinitrile, m. p. 170°) is a mixture of 5- and 8-bromonaphthalene-2-sulphonic acids, mainly the latter; (3) the dinitrile, m. p. 262° from Darmstaedter and Wichelhaus's naphthalenedisulphonic acid (prepared in an unspecified way) is the 1 : 5-isomeride.

The present work makes naphthalene-1 : 2-, -1 : 4-, -1 : 5- and -2 : 6-dicarboxylic acids comparatively accessible for synthetic purposes.

Experiments on the conversion of the dicyanonaphthalenes into benzphthalocyanines are described in the following paper.

EXPERIMENTAL.

1 : 2-*Series*.—(1) Commercial sodium 1-naphthylamine-2-sulphonate gave as good results as material purified through the calcium salt (Erdmann, *Annalen*, 1893, **275**, 226). There was no detectable contamination by the 1 : 4-isomeride. The moist diazo-compound (Cleve, *Ber.*, 1892, **25**, 2475) from 85 g. of the salt was added during 45 minutes to a stirred solution of 108 g. of copper sulphate and 117 g. of potassium cyanide in 650 c.c. of water at 50—60°. After a further 30 minutes at this temperature, 45 g. of sodium chloride were added, the sodium 1-cyanonaphthalene-2-sulphonate (A) was filtered off from the cooled solution and dissolved in very dilute hydrochloric acid, and the potassium salt precipitated by the addition of potassium chloride. This formed pinkish plates from alcohol. Yield, 57 g. (64%) (compare Friedländer and Woroschzoff, *Annalen*, 1912, **338**, 7).

After many preliminary experiments the following general process was used for the cyanide fusion of this salt and its isomerides (compare Brit. Pat. 436,661). A mixture of 25 g. of the cyano-sulphonate and 40 g. of anhydrous potassium ferrocyanide (*ca.* 5 equivs.) was contained in the central portion of a tube of Pyrex glass, 24″ by 1½″, enclosed in an electric furnace 12″ long. One end of the tube was connected to a source of carbon dioxide, the other to a receiver, manometer and pump. The tube sloped very slightly towards the receiver. A slow stream of carbon dioxide was passed, the pressure reduced to about 40 mm., and the temperature raised slowly until a sublimate of dicyanonaphthalene appeared on the cold part of the tube. The temperature was gradually raised as the rate of formation of the product decreased and the process was generally complete in 1—2 hours. The dicyanonaphthalene sublimed in an almost pure condition and no more could be isolated by reheating the residue or extracting it with benzene. The success of the reaction depended upon the efficient transmission of heat through the mass. In the 1 : 2-series a 10 g. batch gave the best yield (75%) and this diminished with batches above 25 g. Addition of metal turnings to conduct the heat led to a slight decrease in the yield, as some pigment of the phthalocyanine type was formed. The reaction occurred at 320—370° with the 1 : 2-cyano-sulphonate and most of its isomerides. Anhydrous sodium and potassium ferrocyanide and sodium cyanide were about equal as reagents; potassium cyanide reacted equally well but at a higher temperature, probably owing to the difference in fusion points. The use of a eutectic mixture of cyanides and the preheating of the carbon dioxide were without advantage. Potassium thiocyanate was unsuitable both as a reagent and as a flux. If potassium ferrocyanide was used in slight excess, the reaction did not proceed so readily but the yield was unaffected; a large excess was without advantage. The ferrocyanide was conveniently dehydrated in the same apparatus at 200°.

Sodium cyanonaphthalenesulphonates were equivalent to the potassium salts. The crude product from the Sandmeyer reaction (such as A above) could be used with advantage for preparative purposes. The overall yield of 1 : 2-dicyanonaphthalene from sodium 1-naphthylamine-2-sulphonate was constant at *ca.* 50% irrespective of the purification of the intermediate.

(2) 200 G. of commercial Tobias acid (2-naphthylamine-1-sulphonic acid) were suspended in hot water and neutralised with sodium carbonate, and the solution filtered, acidified, and cooled. The precipitated acid was crystallised from water, just neutralised with sodium hydroxide, and cooled. β-Naphthylamine was filtered off, and the salt of the amino-acid in the filtrate diazotised either by the method used for naphthionic acid by Erdmann (*Annalen*, 1888, **247**, 329) or by that of Cleve (*loc. cit.*). The diazo-compound was converted into *sodium* 2-*cyanonaphthalene*-1-*sulphonate* by the method already described. Yield, 92% of crude salt, which formed white platelets from alcohol (charcoal) (Found : N, 5·5. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yield of dinitrile from the pure salt was 76% at 320—390°, one batch of 10 g. gave an 84% yield, and the crude Sandmeyer product one of 56%.

Both these preparations gave the same product, which was also identical with that prepared from potassium 1-chloronaphthalene-2-sulphonate (Cleve, *loc. cit.*). With the technique described above, our yields by the last method were about 30%; like Cook (J., 1932, 456), we were unable to obtain the 50% claimed by Waldmann (*J. pr. Chem.*, 1930, **128**, 127). 1 : 2-Dicyanonaphthalene crystallised in white needles, m. p. 190°, from glacial acetic acid, alcohol or petroleum.

5 G. were refluxed for 1½ hours with 70 c.c. of glacial acetic acid, 60 c.c. of concentrated sulphuric acid, and 40 c.c. of water (compare Kay and Morton, J., 1914, **105**, 1571). The solution was cooled and poured into water. Naphthalene-1 : 2-dicarboxylic acid was filtered off and purified by dissolution in sodium carbonate solution, reprecipitation, and crystallisation from water; m. p. 175°, yield 71—74%. The anhydride was readily formed by warming the acid (10 g.) with 10 g. of phosphorus pentachloride in 100 c.c. of phosphorus oxychloride until no more hydrogen chloride was evolved. The product was poured into water and filtered, and the anhydride extracted from the residue with benzene. Yield 85%, m. p. 168°, identical with material prepared by Cleve's method (*loc. cit.*). When the anhydride was fused with half its weight of urea, it gave an almost quantitative yield of 1 : 2-naphthalimide, which sublimed in long yellow needles, m. p. 224°, identical with that prepared, following Cleve, from the diamide. The methyl ester, prepared *via* the silver salt, had m. p. 85°, in agreement with Kruber (*Ber.*, 1932, **65**, 1382). Methylation of the acid with methyl sulphate in sodium hydroxide solution gave the *methyl hydrogen* ester, m. p. 145° (Found : C, 67·6; H, 4·4. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·4%). This was also formed by boiling the anhydride with methyl alcohol for a few minutes.

In the following account we shall indicate only those details in which the preparations differed from those of the 1 : 2-series.*

1 : 3-*Series*.—100 G. of commercial 1-aminonaphthalene-3 : 8-disulphonic acid (ε-acid) yielded 29 g. of pure 1-aminonaphthalene-3-sulphonic acid (Found : N, 6·3. Calc. : N, 6·3%) when reduced by Friedlander and Lucht's method (*Ber.*, 1893, **26**, 3032). The method of Kalle and Co. (D.R.-P. 64979) was less satisfactory.

Diazotisation followed Royle and Schedler (J., 1923, **123**, 1641). The yield of crude *sodium* 1-*cyanonaphthalene*-3-*sulphonate* from the Sandmeyer reaction was 100%, 88%. This was difficult to purify. The best method was extraction (Soxhlet) with methyl alcohol, precipitation with ether, and crystallisation from ethyl alcohol (Found : N, 5·9. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yield of 1 : 3-*dicyanonaphthalene* at 390—400°/100 mm. was 16%, 19% from

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* For additional details, see E. F. Bradbrook, Ph.D. Thesis, London (1935).

pure and 9%, 10% from crude sodium cyano-sulphonate. The product crystallised from acetic acid or alcohol in yellow needles. After sublimation and crystallisation from acetic acid it formed white needles, m. p. 179° (Found: C, 80·7; H, 3·4; N, 15·9. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 15·7%).

2·5 G. were heated under reflux for 1 hour with 50 c.c. of glacial acetic acid, 10 c.c. of water, and 50 c.c. of concentrated sulphuric acid and the naphthalene-1 : 3-dicarboxylic acid was isolated and purified in the same way as the 1 : 2-acid. Yield, 86% of a pale yellow, amorphous solid, m. p. 267—268°.

1 : 4-*Series.*—1-Naphthylamine-4-sulphonic acid was diazotised, following Erdmann (*loc. cit.*). The Sandmeyer reaction yielded 67% of crude sodium 1-cyanonaphthalene-4-sulphonate (A) as pinkish plates very soluble in water. [If potassium chloride were used in the final salting out, a yield of 81% of crude potassium salt (B) was obtained.] The sodium salt was dissolved in hot water, the solution made just acid with hydrochloric acid, and a slight excess of potassium carbonate added. *Potassium* 1-*cyanonaphthalene*-4-*sulphonate* was salted out from the filtered solution by the addition of potassium chloride. It separated from water in small buff crystals (Found: N, 5·4. $C_{11}H_6O_3NSK$ requires N, 5·2%). When fused with potassium ferrocyanide at 320—360°/100 mm., the pure potassium salt gave 71% of 1 : 4-dicyanonaphthalene, the crude potassium salt (B) gave 50%, and the crude sodium salt (A) gave 59%. The dinitrile crystallised from alcohol (charcoal) in long colourless needles, m. p. 208° (Scholl and Neumann, *Ber.*, 1922, **55**, 109, give m. p. 206°).

Hydrolysis yielded 94% of naphthalene-1 : 4-dicarboxylic acid, m. p. above 300°. The methyl ester, obtained from the silver salt, crystallised from dilute acetic acid in long white needles, m. p. 67° (Mayer and Sieglitz, *Ber.*, 1922, **55**, 120, give m. p. 64°).

1 : 5-*Series.*—Naphthalene-1 : 5-disulphonic acid was purified by Fierz-David's method (*Helv. Chim. Acta*, 1923, **6**, 1133). Its barium salt gave 21%, and its sodium salt 12%, of 1 : 5-dicyanonaphthalene when fused with potassium ferrocyanide at 450—580°/50—100 mm.

400 G. of commercial 1-naphthylamine-5-sulphonic acid (Laurent's acid) in 3 l. of hot water were neutralised with sodium carbonate, and the solution filtered and acidified. The precipitated acid was filtered off, washed with hot water, suspended in cold water, and just neutralised with sodium hydroxide. A small amount of sodium 1-naphthylamine-8-sulphonate was removed by filtration, and the filtrate boiled with charcoal and evaporated to dryness. The residual salt was diazotised by Erdmann's method (*loc. cit.*); the damp diazo-compound yielded 65% of crude *sodium* 1-*cyanonaphthalene*-5-*sulphonate*, which formed white needles from alcohol (Found: N, 5·6. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yield of 1 : 5-dicyanonaphthalene was 53% from the pure salt (?) and 56—57% from the crude salt at 330—420° and 40 mm. pressure. It crystallised from glacial acetic acid in white needles, m. p. 262°, not raised by further crystallisation (Scholl and Neumann, *loc. cit.*, give 260°; Moro, *Gazzetta*, 1896, **26**, 92, gives 266°). Hydrolysis yielded 76% of the dicarboxylic acid (m. p. above 300°). The methyl ester crystallised from dilute ethyl alcohol in fine long needles, m. p. 119° (Moro, 114—115°; Radcliffe and Short, J., 1931, 220, 113—114°).

1 : 6-*Series.*—Erdmann (*Annalen*, 1893, **275**, 210) states that 1 l. of boiling methyl alcohol dissolves 0·9 g. of calcium 1-naphthylamine-6-sulphonate and 13 g. of the 1 : 7-isomeride. Commercial Cleve's acid (1 : 6-, 1 : 7-, and a little 1 : 3-) was neutralised mainly with calcium hydroxide and completely with calcium carbonate. The excess of carbonate was removed, and the solution evaporated to dryness. 100 G. of the calcium salt were extracted (Soxhlet) with 1½ l. of boiling methyl alcohol, until about 5 g. of solid separated from the extract. The extract was filtered and evaporated to dryness, 20 g. of calcium salt, containing mainly the 1 : 7-isomeride, being obtained (A). The residue in the extractor was extracted with fresh methyl alcohol for the same time and finally boiled with 500 c.c. of methyl alcohol to free it completely from the 1 : 7-salt. These extracts were rejected. The calcium salt of the 1 : 6-acid so obtained, treated in the manner described for the 1 : 2-isomeride, yielded 88% of crude sodium 1-cyanonaphthalene-6-sulphonate. The Sandmeyer product contained inorganic matter (cuprous cyanide ?) which could not be removed by crystallisation but was partly eliminated by continuous extraction with methyl alcohol, in which the cyano-sulphonate was more soluble.

Commercial 1-naphthylamine-6-sulphonic acid was suspended in hot water and neutralised with sodium carbonate, and the solution filtered and acidified with hydrochloric acid. The acid which crystallised from the cold solution (100% by titration with standard sodium nitrite) was converted into potassium 1-cyanonaphthalene-6-sulphonate in the usual way. This also contained inorganic impurity and was partly purified as before.

On fusion with potassium ferrocyanide at 340—390°/90 mm. the cyano-sulphonate from the calcium salt gave an 11% yield of dicyanonaphthalene, that from the commercial acid an 18% yield. Neither product was the pure 1 : 6-isomeride and the separation described above was therefore incomplete. Crystallisation from alcohol gave material of m. p. 165—175°; this was extracted with boiling petroleum, and the residue crystallised from glacial acetic acid and sublimed. Pure 1 : 6-dicyanonaphthalene was then obtained as white needles, m. p. 211° (Weissgerber and Kruber, *loc. cit.*, 208—210°). A small amount of what appeared to be crude 1 : 3-isomeride was obtained from the mother-liquors.

Methyl naphthalene-1 : 6-dicarboxylate formed white needles from dilute alcohol, m. p. 97—98° (Meyer and Bernhauer, *Monatsh.*, 1929, **53**, 721, 98°).

1 : 7-*Series*.—120 G. of crude calcium 1-naphthylamine-7-sulphonate [such as (A) above] were extracted with boiling methyl alcohol until only about 20 g. remained. The extract yielded, after repetition of this procedure, 90 g. of practically pure 1 : 7-salt, which gave 67 g. of crude sodium 1-cyanonaphthalene-7-sulphonate, contaminated with inorganic impurity. It was partly purified by extraction with alcohol (sample *a*).

A solution of 200 g. of commercial sodium 1-naphthylamine-7-sulphonate in 2 l. of hot water was filtered and acidified with hydrochloric acid. The acid which crystallised on cooling was 99% pure by titration with sodium nitrite. 200 G. yielded 170 g. of crude sodium 1-cyanonaphthalene-7-sulphonate (sample *b*).

Samples *a* and *b* of this salt gave 19% and 30% yields respectively of 1 : 7-*dicyanonaphthalene* when fused with potassium ferrocyanide at 340—450°/50 mm. Unlike the 1 : 6-dinitrile, both products were practically free from isomeric impurity. 1 : 7-Dicyanonaphthalene crystallised from alcohol, dilute acetic acid, or light petroleum (b. p. 80—100°) in white needles, m. p. 167° (Found : C, 81·1; H, 3·5; N, 15·8. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 15·7%). It gave a 98% yield of the corresponding acid, the methyl ester of which crystallised from dilute alcohol in white plates, m. p. 90° (cf. Ruzicka and van Melsen, *loc. cit.*).

1 : 8-*Series*.—1-Naphthylamine-8-sulphonic acid (*peri*-acid) yielded 77% of crude *sodium 1-cyanonaphthalene-8-sulphonate*. This contained a persistent red impurity, which was removed by repeated crystallisation from a little water, the solution being decolorised with zinc dust and acetic acid (Found : N, 5·3. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The pure salt gave a 9% yield of 1 : 8-*dicyanonaphthalene* at 360—400°/80 mm. The dinitrile was best purified by sublimation, followed by crystallisation from alcohol, which yielded white needles, m. p. 232° (Found : C, 81·2; H, 3·6; N, 15·6. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 15·7%).

The dinitrile was obtained in rather better yield * by fusing recrystallised potassium 1-cyanonaphthalene-8-sulphonate with an equal weight of dry potassium cyanide for 1 hour at 400°/30 mm. The yield of crude dinitrile was 27%; m. p. 230° after successive crystallisations from alcohol and petroleum (b. p. 100—120°).

On hydrolysis with warm sulphuric acid the dinitrile yielded naphthalic anhydride (long needles from alcohol, m. p. 262°). Methyl naphthalate, made by means of methyl sulphate, formed long needles from dilute methyl alcohol, m. p. 104° (lit., 102—104°).

2 : 6-*Series*.—Sodium 2-naphthylamine-6-sulphonate (100 g., made from commercial Brönner's acid) was suspended in 500 c.c. of water and treated successively with 225 c.c. of concentrated hydrochloric acid and a solution of 30 g. of sodium nitrite in 250 c.c. of water. This diazo-compound was more soluble than its isomerides and the entire liquor from the above was therefore neutralised with sodium carbonate and treated with cuprocyanide solution from 125 g. of copper sulphate and 132 g. of potassium cyanide in 1 l. of water. The addition of 400 g. of sodium chloride liberated crude *sodium 2-cyanonaphthalene-6-sulphonate* (65%), which formed slightly pink plates from water (charcoal) (Found : N, 5·5. $C_{11}H_6O_3NSNa$ requires N, 5·5%). The yields of dicyanonaphthalene were 42% from the pure salt and 29% from the crude at 350—450°/50 mm. 2 : 6-Dicyanonaphthalene crystallised from acetic acid (charcoal) in white needles, m. p. 293° (Ebert and Mertz, *Ber.*, 1876, **9**, 604, give m. p. 297°). The acid obtained on hydrolysis (91% yield, m. p. above 300°), gave through the silver salt a methyl ester, which formed plates from alcohol, m. p. 186° (lit., 187—191°).

2 : 7-*Series*.—Sodium 2-naphthylamine-7-sulphonate (from amino-F-acid), diazotised according to Butler and Royle (J., 1923, **123**, 1649), yielded 80% of crude *sodium 2-cyanonaphthalene-7-sulphonate*, which crystallised from concentrated aqueous solution, in the presence of a little zinc and acetic acid, in pale yellow needles (Found : N, 5·5. $C_{11}H_6O_3NSNa$ requires N, 5·5%). 2 : 7-Dicyanonaphthalene was obtained in 7·5% yield from the pure, and 5% yield from the

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* This experiment was carried out by Dr. A. R. Lowe.

crude salt at 350—400°/35 mm. After sublimation it crystallised from glacial acetic acid in white needles, m. p. 267°, in agreement with Ebert and Mertz (*loc. cit.*). The methyl ester of the corresponding acid formed long needles from methyl alcohol, m. p. 135°, in agreement with Kaufler and Thien (*Ber.*, 1907, **40**, 3258).

2 : 3-*Series* (with A. R. LOWE).—Commercial 2-amino-3-naphthoic acid, purified through the hydrochloride, was diazotised and treated by the Sandmeyer reaction following Waldmann (*loc. cit.*). The product after sublimation had m. p. 273° alone or mixed with 2 : 3-naphthalimide prepared by fusing 2 : 3-naphthalic anhydride with urea (Freund and Fleischer, *loc. cit.*, give m. p. 275° for this imide). 2 : 3-Naphthalimide was sublimed in a rapid stream of ammonia through a hard-glass tube containing thoria electrically heated to 490°. The neutral product was freed from imide and anhydride with caustic alkali and crystallised from alcohol. 2 : 3-*Dicyanonaphthalene* crystallised in shining white needles, m. p. 251° (Found : C, 80·7; H, 3·6; N, 15·8. $C_{12}H_6N_2$ requires C, 80·9; H, 3·4; N, 15·7%). Naphthalene-2 : 3-dicarboxylic acid yielded through the silver salt the *methyl* ester, which formed large plates on evaporation of its solution in ether–light petroleum, m. p. 47° (Found : C, 69·3; H, 4·9. $C_{14}H_{12}O_4$ requires C, 68·9; H, 4·9%).

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