XVI.—*The Nitration of β-Naphthoic Acid and Some New Amino- and Nitro-naphthoic Acids.*

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The Nitration of β-Naphthoic Acid.

THE earliest work on the nitration of β-naphthoic acid was carried out by Kuchenmeister (*Ber.*, 1870, **3**, 740), and by Ekstrand (*ibid.*, 1879, **12**, 1393), but yielded little if anything of permanent value. Later, Ekstrand (*J. pr. Chem.*, 1890, **42**, 273), by fractional crystallisation of the mixture of ethyl esters obtained from the crude nitration product, isolated five supposedly distinct compounds. Of these, one (m. p. 111°) gave a free acid, m. p. 295°, which was identical with that previously prepared by Graeff (*Ber.*, 1883, **16**, 2252) from the nitration product of β-naphthonitrile, and was shown to be 8-nitro-2-naphthoic acid. The second ester (m. p. 121°; free acid, m. p. 288°) was that of 5-nitro-2-naphthoic acid. From the small fractions which remained, one ester melting at 75° was isolated (free acid, m. p. about 285°), and two others were described in the following year (*ibid.*, 1891, **43**, 409); of these, one melted at 92° (free acid, m. p. 272° [279°] *) and the other at

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* This nitro-acid on reduction gave an aminonaphthoic acid, m. p. 211°. Now 5-amino-1-naphthoic acid melts at this temperature, and the 5-nitro-isomeride is to be expected from the nitration of α-naphthoic acid, if any occurred as impurity in Ekstrand's initial material. Further, 8-nitro-1-naphthoic acid, which would also be formed, cannot be esterified by the method employed (hydrogen chloride in alcoholic solution; compare Ekstrand, *ibid.*, 1888, **38**, 156) and therefore would not appear in the esterified mixture. Finally, the ethyl ester of 5-amino-1-naphthoic acid melts at 92° (compare above). The free nitro-acid, however, melts at 242° (Graeff, *loc. cit.*, p. 2250).

131°. (This last ester charred when warmed with sulphuric acid in the usual way, and the corresponding nitro-acid was not isolated.) No constitutions were assigned by Ekstrand to these isomerides.

Of the seven possible mononitro-derivatives of β-naphthoic acid, Ekstrand had thus claimed to have detected the presence of five. These did not include the 1-nitro-compound, m. p. 239°, which has since been prepared by Mayer and Oppenheimer (*Ber.*, 1918, **51**, 1239). The characteristics of this derivative as described by these authors do not coincide with those of any of Ekstrand's supposed nitronaphthoic acids.

Repetition of Ekstrand's experiments, using his second method of nitration (*i.e.*, in absence of any solvent), has shown that approximately equal amounts of 5- and 8-nitro-2-naphthoic acids are formed in at least 95% combined yield. Some low-melting indeterminate fractions of the esters resulting from the use of alcohol or benzene as crystallising medium were all easily resolved by employing ethyl acetate and light petroleum. With regard to Ekstrand's highest-melting ester (m. p. 131°) which charred with sulphuric acid, it is to be noted that the ethyl ester of 7-nitro-2-naphthoic acid (prepared by the present authors at a later stage) melts at 131°, but can be hydrolysed quite easily to give a quantitative yield of the nitro-acid. No trace of this ester was detected in the nitration product.

In addition to the 5- and 8-nitro-isomerides, we have succeeded in establishing the presence of traces of 1-nitro-2-naphthoic acid in the nitration mixture.* This acid cannot be esterified by the passage of hydrogen chloride into an alcoholic solution, and consequently was easily separated from the reaction material. It was never obtained quite pure, but reduction with ferrous sulphate and ammonia produced an aminonaphthoic acid, m. p. 202—205° (decomp.), the *acetyl* derivative of which crystallised from alcohol in long, gorse-like needles, m. p. 184°. This was identical with an authentic specimen of 1-acetylamino-2-naphthoic acid prepared synthetically (see Friedländer and Littner, *Ber.*, 1915, **48**, 330).

During the nitration of β-naphthoic acid, therefore, between 60—80° with excess of nitric acid (*d* 1·42) only 5-nitro-2-naphthoic acid (m. p. 291° instead of 288°) and 8-nitro-2-naphthoic acid

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* Ekstrand (*ibid.*, 1890, **42**, 273) digested the mixture of nitro-acids with sodium hydroxide during an attempt to separate them by fractionation of their sodium salts. But Friedländer and Littner (*Ber.*, 1915, **48**, 330) have proved that hydrolysis of 1-nitro-2-naphthonitrile by alkaline reagents (even barium hydroxide) causes the replacement of the nitro-group by a hydroxyl group, and this also takes place in the case of the acid. It is therefore probable that Ekstrand had destroyed any 1-nitro-compound present.

(m. p. 295°) are formed in large quantity, together with a trace of 1-nitro-2-naphthoic acid.

Some New Amino- and Nitro-naphthoic Acids.

Of the seven theoretically possible amino-derivatives of α-naphthoic acid, only four (the 2-, 4-, 5-, and 8-amino-1-naphthoic acids) have hitherto been prepared. Even fewer of the nitro-α-naphthoic acids are known, since no compound containing one nitro-group in any of the four β-positions is recorded. Of the substituted derivatives of β-naphthoic acid, only one amino-acid, the 6-derivative, had not been prepared, but there were still four unknown nitro-isomerides, *viz.*, the 3-, 4-, 6- and 7-nitro-2-naphthoic acids.* As a result of the present work, 6- and 7-amino-1-naphthoic acids, 6-amino-, 6- and 7-nitro-2-naphthoic acids have been obtained for the first time.

The method adopted for the preparation of these aminonaphthoic acids consists in heating the neutral sodium salt of the corresponding hydroxynaphthoic acid † with ammonia and bisulphite under pressure. Möhlau and Kriebel (*Ber.*, 1895, **28**, 3096) had already employed strong ammonia (without bisulphite) to convert 3-hydroxy-2-naphthoic acid into the amino-acid. Repetition of their experiment, however, showed no appreciable conversion, either with the 3-isomeride or any other. Neither could the 3-amino-compound be obtained when bisulphite was used, though the conditions were varied over a wide range. β-Naphthylamine was the sole product of reaction, as it was also from the anilide of 3-hydroxy-2-naphthoic acid (naphthol A.S.). Similarly, 1-hydroxy-2-naphthoic acid yielded α-naphthylamine.

In addition to the new aminonaphthoic acids mentioned, 5- and 8-amino-2-naphthoic acids have also been prepared by the use of the bisulphite modification.

All the amino-2-naphthoic acids thus obtained were converted into nitronaphthoic acids by treatment of the diazotised product with copper powder and excess of sodium nitrite, as described by Veselý and Dvořak (*Bull. Soc. chim.*, 1922, **31**, 421; 1923, **33**, 319). The 5- and 8-nitro-2-naphthoic acids so prepared were used

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* Mention is made (A., 1923, **124**, i, 119) of a nitronaphthoic acid, m. p. 225—227°, obtained by Ruzicka and Stoll (*Helv. Chim. Acta*, 1922, **5**, 923) as a by-product in the oxidation of 2-methyl-8-*iso*propylnaphthalene with dilute nitric acid, the main product being 2 : 8-naphthalenedicarboxylic acid. The nitronaphthoic acid in question is really a nitro-8-*iso*propyl-2-naphthoic acid; the abstract is somewhat misleading.

† For the details of preparation of the various hydroxynaphthoic acids see Butler, Royle, and Schedler (J., 1923, **123**, 1641, 1649).

to confirm the identity of the nitration products of β-naphthoic acid (see previous section).

EXPERIMENTAL.

Conversion of Hydroxy-acids into Amino-acids.—The hydroxynaphthoic acid (15 g.) is dissolved in water with the aid of sodium bicarbonate (6·3 g.); ammonia (100 c.c., *d* 0·88) is added, followed by a solution, saturated at 15°, of sulphur dioxide in water (25 c.c.). The whole is diluted with water (110 c.c.), and heated in an autoclave at 200—210° (pressure about 50 atmospheres) for 10 hours. The solution is boiled to drive off most of the ammonia, filtered, and slightly acidified by the gradual addition of acetic acid. Under these conditions 5- and 8-amino-2-naphthoic acids separate in a very satisfactory condition. With 6-amino-2-naphthoic acid (and to a less extent with 6- and 7-amino-1-naphthoic acids) it is advisable to add an excess of warm dilute hydrochloric acid to the acetic acid solution. After extraction with ether to remove impurities, the solution is concentrated and the amino-hydrochloride allowed to crystallise. The free acid is regenerated by dissolving in a small quantity of sodium carbonate solution and carefully neutralising with acetic acid. 7-Amino-2-naphthoic acid is best isolated through its difficultly soluble sodium salt, by the addition of sodium hydroxide to the autoclave liquor after removal of excess of ammonia. The yield in every case is almost theoretical.

The various aminonaphthoic acids differ but slightly from one another as regards their solubilities. They are easily soluble in alcohol or acetic acid, somewhat less easily soluble in ether, acetone or ethyl acetate, and very sparingly soluble in benzene.

6-*Amino*-1-*naphthoic acid* crystallises from alcohol in light brown aggregates, m. p. 203° (Found: C, 70·4; H, 4·8. $C_{11}H_9O_2N$ requires C, 70·6; H, 4·8%). The *hydrochloride* crystallises from water in clumps of needles, and the *acetyl* derivative from alcohol in white needles, m. p. 170—172°.

7-*Amino*-1-*naphthoic acid* crystallises from alcohol in light brown prisms, m. p. 223—224° (Found: C, 70·3; H, 5·0%). The *hydrochloride* separates from water in warty clusters of needles, and the *acetyl* derivative from alcohol in almost white needles, m. p. 229—230°.

6-*Amino*-2-*naphthoic acid* crystallises from dilute alcohol in very pale yellow needles, m. p. 225° * (Found: C, 70·8; H, 4·7%).

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* Since this work was completed a compound described as "6-amino-2-naphthoic acid" has been obtained by Dziewoński, Schoenówna, and Waldmann (*Ber.*, 1925, **58**, 1211). These authors give the melting point as 222—223°; but the acetyl derivative, from which the free amino-acid

The *hydrochloride* is not very soluble in cold but rather more soluble in hot water, crystallising in small flakes. The *acetyl* derivative separates from dilute alcohol or from acetone in white needles, m. p. 230—232°.

7-Amino-2-naphthoic acid crystallises from alcohol in pale yellow leaflets, m. p. 245°. Its *acetyl* derivative separates from dilute alcohol in almost white, flat needles, m. p. 200—201° (decomp.).*

Types of Fluorescence shown.

Solvent.	α : 6-.	α : 7-.	β : 4-.	β : 5-.	β : 6-.	β : 7-	β : 8-.
Alcohol	Green	Emerald green	Blue	Green	Purple	Sea green	Emerald green
Ether	Light blue	Emerald green	Royal blue	Cobalt blue	Purple	Pale blue	Turquoise blue
Acetic acid	Pale violet	Bluish-green	(Blue)	(Green)	Cobalt blue	Bluish-purple	Leaf green
Benzene	Royal blue	Sky blue	Bluish-purple	Light blue	Violet blue	(Blue)	Greenish-blue
Ethyl acetate	Turquoise blue	Turquoise blue	Blue	Greenish-blue	Reddish-violet	Blue	Bluish-green
Acetone	Greenish-blue	Turquoise blue	Royal blue	Turquoise blue	Reddish-violet	Blue	Bluish-green

A few of these fluorescences require magnesium light or the light from an iron arc to render them visible; such are indicated by brackets. The majority are very marked, even in subdued daylight. The colours given in the table are those induced by arc light; they vary slightly in one or two instances from the fluorescences in daylight.

In addition to the preceding observations on the fluorescent properties of aminonaphthoic acids taken under approximately standard conditions, 1-amino-2-naphthoic acid furnishes an appreciable blue fluorescence in alcohol, ether, or acetic acid, while 3-amino-2-naphthoic acid (according to Möhlau and Kriebel, *loc. cit.*) gives a green fluorescence in alcohol or ether.

It is worthy of note that the aminonaphthoic acids whose configurations correspond to those of possible naphthaquinones produce more intensely fluorescent solutions than those not having a potentially quinonoid structure; *e.g.*, β : 8- is stronger than β : 5-; β : 6- than β : 7-; and α : 7- than α : 6-.

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was prepared, melts at 271—272°. It is to be observed that the configuration of this isomeride was only arrived at by a process of exclusion. On the other hand, the constants given do not coincide with those of any other amino-2-naphthoic acid, all of which are now known.

* It is important to carry out the melting-point determinations of these acetyl derivatives in a standardised manner, in order to ensure concordant results. No method other than the one here described gives a definite fluid melt. The tube is inserted when the temperature of the bath is only about 5° below the expected m. p. of the substance, and the time taken for the necessary rise in temperature must be less than 2 minutes. Incipient softening usually precedes liquefaction, and on increasing the temperature the substance reverts to the solid state, melting a second time, though not sharply, at a somewhat higher temperature. (To suggest that the m. p.—271—272°—recorded in the previous note is really this higher melting point would be somewhat premature, since the range is limited to 1°.)

Conversion of Amino-acids into Nitro-acids.—The aminonaphthoic acid (8 g.) is dissolved in warm glacial acetic acid (30 g.), and sulphuric acid (16 g.), diluted with an equal volume of water, added with constant stirring. The sulphate which separates is at once diazotised at 0° with sodium nitrite (3·5 g.) dissolved in water (15 c.c.). The clear diazo-solution is poured in small portions into a solution of sodium nitrite (35 g. in 140 c.c. of water) containing also clean copper bronze (30 g.). The reaction liquor, on standing at room temperature for 4 hours with regular shaking, deposits the whole of the nitronaphthoic acid, which is filtered off and purified by repeated extractions with boiling alcohol (charcoal). The filtered alcoholic solution is concentrated to a small bulk; the addition of water then precipitates the nitronaphthoic acid as a yellow powder. The total yield is about 0·5 g.

6-*Nitro*-2-*naphthoic acid* crystallises from alcohol in pale yellow plates, m. p. 310° (Found: C, 60·5; H, 3·4. $C_{11}H_7O_4N$ requires C, 60·8; H, 3·2%). The *ethyl* ester, m. p. 177°, crystallises in brownish-yellow, rectangular plates from ethyl acetate, in needles from alcohol. The acid can be recovered from the ester by hydrolysis with strong sulphuric acid on the water-bath for a few hours.

7-*Nitro*-2-*naphthoic acid* crystallises from alcohol in yellow needles, m. p. 262° (Found: C, 60·6; H, 3·4%). It is moderately soluble in acetic acid, but dissolves with difficulty in other solvents. The *ethyl* ester crystallises from alcohol in pale salmon-coloured, silky needles, m. p. 131°. This ester shows no sign of charring when hydrolysed with sulphuric acid in the usual way (compare Ekstrand's ester, m. p. 131°; see p. 85).

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