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CONDENSATION OF 2,4-DINITROCHLOROBENZENE WITH *o*-HYDROXYARYLAMIDES*

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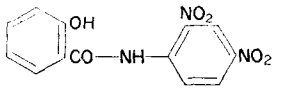
Abstract—*o*-Hydroxyarylamides react readily with 2,4-dinitrochlorobenzene in presence of bases to give the N-2,4-dinitrophenyl derivatives. The reaction appears to proceed by a direct displacement of the halogen by the amide nitrogen involving intramolecular nucleophilic catalysis by the phenoxide oxygen; but a Smiles rearrangement is not completely excluded. The N-dinitrophenyl derivatives are stable to boiling hydrochloric acid, but are hydrolysed easily by aqueous sodium carbonate or hydroxide. Condensation with dinitrochlorobenzene, followed by mild alkaline hydrolysis, is a useful procedure for determining the constitution of azoic coupling components of the Naphtol AS type. Thus Naphtol AS-RS and AS KN have been shown to be the 4-chloro-2-methoxy-5-methylanilide of 2-hydroxy-3-naphthoic acid and the α-naphthylamide of 3-hydroxydibenzofuran-2-carboxylic acid respectively.

THE Sanger method for determining the amino acid sequence in a protein depends on the condensation of 2,4-dinitrofluorobenzene (DNFB) with free amino groups at room temperature in sodium bicarbonate solution, leaving amide groups unaffected, and on the subsequent hydrolysis of the terminal amide group by hydrochloric acid.[1] Since *o*-hydroxybenzanilides condense with cyanuric chloride, the amide nitrogen and not the phenolic oxygen being attacked,[2] it appeared probable that they would react similarly with DNFB. The amide groups in salicylamide, salicylanilide and 2-hydroxy-3-naphthanilide have now been found to react readily with DNFB in presence of ethanolic sodium hydroxide at about 50° or triethylamine in dimethylformamide (DMF)[3] at room temperature. The amide group in benzamide and benzanilide are unreactive towards DNFB as well as cyanuric chloride; and likewise the hydroxyl group in *p*-hydroxybenzanilide is attacked by both the reagents. In the Sanger procedure DNFB is preferred to the much commoner DNCB, because the latter requires heat for the condensation, resulting in a certain amount of hydrolysis of the protein.[1,4] DNCB, however, is adequate for the reaction with *o*-hydroxybenzamides; the products (I, II, III) are in fact more easily crystallizable than those obtained when DNFB is used.

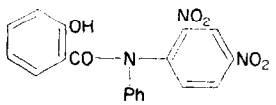
The inability of an amide group to react with DNCB is the result of the amide resonance (IVA ⟷ IVB) and the consequent lowering of the basicity or nucleophilic reactivity of the nitrogen atom. In the amide or anilide of salicylic acid the amide resonance is weakened considerably by the participation of the CO group in a chelate ring, stabilized by resonance between structures VA and VB.

* Communication No. 409 from the National Chemical Laboratory, Poona, India.

[1] F. Sanger, *Biochem. J.* **39**, 507 (1945).
[2] B. S. Joshi, R. Srinivasan, R. V. Talavdekar and K. Venkataraman, preceding paper.
[3] M. L. Wolfrom, B. O. Julian, M. S. Toy and A. Chaney, *J. Amer. Chem. Soc.* **81**, 1446 (1959).
[4] E. Abderhalden and W. Stix, *Hoppe-Seyler's Z.* **129**, 143 (1923).



I



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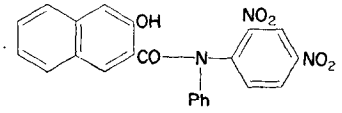
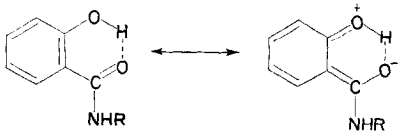


III

IV A IV B

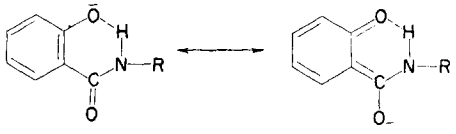


V A V B

The basicity of the nitrogen atom is therefore greater than in benzamide, and a nucleophilic attack on DNCB becomes possible. In the absence of sodium hydroxide, when the above mechanism may be pictured, the reaction proceeds very slowly; the yield of the dinitrophenyl derivative (III) is only about 5 per cent in boiling nitrobenzene after 4 hours.

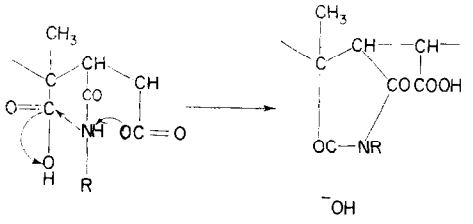
Another conceivable explanation for the reactivity of the amide nitrogen is that hydrogen bonding of an amide hydrogen with the phenolic oxygen in the transition state for the displacement may lower the activation energy for the reaction. An *o*-methoxyl group should then be more effective than an *o*-hydroxyl in increasing the reactivity. It was found however that the anilide of *o*-methoxybenzoic acid did not react with DNCB.

The reactivities observed when this reaction takes place in the presence of a base are very much greater, indicating the operation of a different mechanism. The reaction may proceed either by a direct attack of DNCB on the amide nitrogen or through the prior formation of the diphenyl ether and subsequent migration of the dinitrophenyl group to the amide nitrogen atom. In alkaline solution *o*-hydroxybenzamides and *o*-hydroxybenzanilides will exist in the conformation indicated in VIA and VIB, wherein the oxygen atoms carrying partial negative charges are farthest apart and there is hydrogen bonding between the phenolic oxygen and the amide hydrogen atoms.

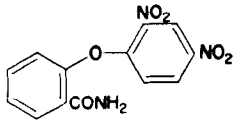


VI A VI B

The affinity of the anion of 2-hydroxy-3-naphthanilide for cellulose has been explained on the basis of similar structures[5]. The nucleophilic reactivity of the amide nitrogen in these cases may be expected to be of the same order as that of amines, and a reasonable mechanism for the reaction is the direct displacement of the halogen from DNCB by the amide nitrogen. The interaction between the phenoxide oxygen and the amide hydrogen will be stronger in the transition state for the reaction than in the species (VI) itself. Intramolecular nucleophilic catalysis of this type has been observed by Zimmering *et al.*[6] in a study of the rate of imidization of a copolymer of methacrylic acid with maleic anhydride, which was treated with *p*-nitroaniline. The anilide groups are surrounded by β-carboxylic acid groups on either side in the polymer chain. The velocity of imidization goes through a maximum at pH 5 and corresponds to the following mechanism for the reaction.[6,7]



A hydrogen bridge of this type cannot occur in the transition state for the reaction of *p*-hydroxybenzanilide with DNCB. The amide nitrogen atom therefore remains inactive and the phenoxide end of the molecule makes the normal nucleophilic attack on DNCB leading to the formation of the dinitrophenyl ether.



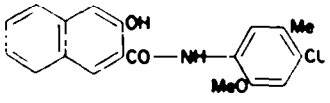
VII

The alternative path for the reaction may now be briefly considered and compared with the mechanism already discussed. Tozer and Smiles[8] prepared the 2,4-dinitrophenyl ether (VII) of salicylamide by condensing methyl salicylate with DNCB in presence of sodium methoxide in methanol, and converting the ester to the amide via the acid and acid chloride; they found that VII rearranged to salicyl-2,4-dinitroanilide (I) by treating with a solution of sodium hydroxide in aqueous acetone at 18° for 2 minutes or by heating it at 200°. They also synthesized I by shaking DNCB with an ethanolic solution of salicylamide and sodium ethoxide. A mechanism involving a Smiles rearrangement looks entirely plausible for the reaction under discussion. In an attempt to choose between these two mechanisms we have determined the relative reactivities of salicylanilide, *p*-hydroxybenzanilide, N-methylsalicylanilide and aniline towards DNCB in dimethylformamide in presence of triethylamine. It has been found that N-methylsalicylanilide and *p*-hydroxybenzanilide react to the extent

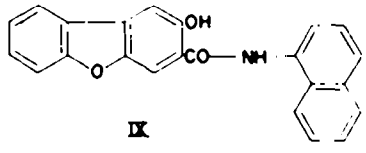
[5] K. Venkataraman, *The Chemistry of Synthetic Dyes* Vol. I, p. 681. Academic Press, New York (1952).
[6] E. W. Westhead, Jr. and H. Morawetz, *J. Amer. Chem. Soc.* **80**, 237 (1958); P. E. Zimmering, E.W. Westhead, Jr. and H. Morawetz, *Biochim. Biophys. Acta* **25**, 376 (1957).
[7] M. L. Bender, *Chem. Rev.* **60**, 87 (1960).
[8] B. T. Tozer and S. Smiles, *J. Chem. Soc.* 2052 (1938).

of 13 per cent and 34 per cent respectively in one hour at about 66°. Under the same conditions aniline undergoes 45 per cent reaction. The normal phenoxide reactivity towards DNCB which is greater than that of aniline is found to be depressed strongly by the presence of carbonyl groups in the *ortho* and *para* positions. This lowering of reactivity is greater in the *o*-isomer because of the additional steric factor involved. If the second mechanism involving a Smiles rearrangement is operating in the reaction, it may be expected that the reactivity of salicylanilide will be less than that of *p*-hydroxybenzanilide and close to that of N-methylsalicylanilide.* Actually we find that salicylanilide gives under comparable conditions about 53 per cent of the N-dinitrophenyl derivative, which exceeds by more than 50 per cent the reactivity of *p*-hydroxybenzanilide and is even greater than that of aniline. This is the kind of behaviour to be expected from the first mechanism involving intramolecular nucleophilic catalysis. It should be mentioned that there are side reactions accompanying the formation of the N-dinitrophenyl derivative from salicylanilide. The amount of DNCB used up in the reaction, when an equimolecular proportion of the reagents was employed, was measured by estimating the chloride liberated and corresponds to 88 per cent reaction.

Like the cyanuric chloride derivatives the N-dinitrophenyl derivatives are readily hydrolysed by alkali, but they are very stable to acid. By heating with 1 per cent aqueous sodium hydroxide at 75–80° for 3 hours or refluxing with 10 per cent aqueous sodium carbonate for 14 hours the hydrolysis of III to 2-hydroxy-3-naphthoic acid and 2,4-dinitrodiphenylamine is complete. One advantage of the dinitrophenyl derivatives from the point of view of using them for determining the constitution of azoic coupling components of the Naphtol AS type is that the aromatic amine moiety is isolated as the brightly coloured dinitrodiphenylamine which crystallizes readily and is also suitable for chromatography on alumina. Thus by condensation with DNCB and subsequent hydrolysis two of the recently introduced Naphtols, AS-RS (C.I. Azoic coupling component 28) and AS-KN (C.I. Azoic coupling component 37) have been found to be constituted as VIII and IX. The former is highly substantive to cellulose and gives fast red shades with suitable diazonium salts; the latter gives dark grey to dark brown shades.



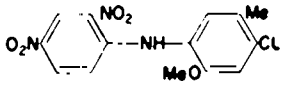
VIII



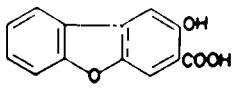
IX

Naphtol AS-RS, $C_{19}H_{16}O_3NCl$, contains a methoxyl group. Hydrolysis of the dinitrophenyl derivative gave 2-hydroxy-3-naphthoic acid and the N-dinitrophenyl derivative (X) of 3-amino-4-methoxy-6-chlorotoluene (chlorocresidine), from which the constitution of VIII followed and was confirmed by synthesis. Similarly the dinitrophenyl derivative of Naphtol AS-KN gave on hydrolysis 3-hydroxydibenzofuran-2-carboxylic acid (XI) and N-2,4-dinitrophenyl-α-naphthylamine; (XI) was identified by comparison with the acid obtained in a similar manner from Naphtol AS-BT (C.I. 37605), which is known to be the 2,5-dimethoxyanilide of XI.

* In this case the formation of *o*-dinitrophenyl derivative should be rate-determining since the second step involving the Smiles rearrangement is known to be very fast.



X



XI

EXPERIMENTAL

N-(2',4'-Dinitrophenyl)-2-hydroxy-3-naphthanilide (III)

(a) A solution of 2-hydroxy-3-naphthanilide (1 g) in ethanol (50 ml) and 10% NaOH (1·5 ml) was added in 15 min to a stirred solution of DNFB (1 g) in ethanol (20 ml) at 50°. After stirring for 2 hr at 50–55°, the solution was poured into water (100 ml) and left overnight. The yellow precipitate crystallized from ethanol (Norit) in pale yellow plates (1·3 g), m.p. 183°, raised to 194° after 3 crystallizations. (Found: C, 64·8; H, 3·8; N, 9·6. $C_{23}H_{15}O_6N_3$ requires: C, 64·3; H, 3·5; N, 9·8%).

(b) When the above reaction was carried out with DNCB (1·2 g) for 3 hr at 65–70°, the product (0·9 g) melted at 194° after one crystallization. A slightly better yield was obtained by shaking the mixture at 35° for 18 hr.

(c) A solution of 2-hydroxy-3-naphthanilide (5 g) in DMF (50 ml) was shaken with DNCB (5 g) and triethylamine (3 ml) for 24 hr at 25° and then poured into water (400 ml). Crystallization of the precipitate successively from chlorobenzene and benzene–hexane gave yellow plates (5·2 g), m.p. 194°.

(d) 2-Hydroxy-3-naphthanilide (1·3 g), DNCB (1·1 g) and anhydrous potassium carbonate (0·35 g) were refluxed in methyl ethyl ketone (100 ml) for 17 hr. The solvent was distilled off, and the residue treated with water. The brownish red solid crystallized from ethanol in pale yellow plates (0·81 g), m.p. 194°.

N-(2',4'-Dinitrophenyl)-salicylanilide (II)

(a) A solution of salicylanilide (0·84 g) in ethanol (25 ml) and 10% NaOH (1·6 ml) was refluxed with DNCB (1 g) for 3 hr. Dilution with water and ether extraction led to an oil, which was obtained crystalline from ethanol–acetone by slow cooling. The yellow needles (0·55 g) shrank at 75° and melted at 145°. (Found: C, 59·7; H, 4·0; N, 10·3. $C_{19}H_{13}O_6N_3$, C_2H_5OH requires: C, 59·3; H, 4·5; N, 9·9%).

(b) A solution of salicylanilide (2·1 g), DNFB (1·2 ml) and triethylamine (1·5 ml) in DMF (10 ml) was shaken at 25° for 24 hr and then poured into water (100 ml). The precipitate crystallized from benzene–hexane (Norit) in pale yellow prisms (1·2 g), m.p. 145°.

(c) When DNFB was replaced by DNCB (2·2 g) in (b), the yield of II was 2·25 g.

(d) To a refluxing solution of salicylanilide (1·06 g) and sodium bicarbonate (0·42 g) in ethanol (25 ml) a solution of DNCB (1·04 g) in ethanol (50 ml) was added over 15 min, and refluxing continued for 3 hr. The solution was poured into water (250 ml) and made slightly acidic with conc HCl. The solution was extracted with ether, and the oil obtained after removal of ether crystallized from ethanol in yellow needles (0·78 g), m.p. 145°, after shrinking at 76°.

(e) Salicylanilide (0·852 g), DNCB (0·81 g) and anhydrous potassium carbonate (0·14 g) were refluxed in acetone (50 ml) for 4 hr and poured into water (200 ml). Worked up as above, the yield was 0·72 g.

p-(2',4'-Dinitrophenoxy)-benzanilide

p-Hydroxybenzanilide (0·6 g), DNCB (0·7 g) and triethylamine (0·5 ml) were dissolved in DMF (10 ml) and shaken for 24 hr at 25°. The solution was poured into water (200 ml) and a few drops of conc HCl. The precipitate crystallized from acetone in colourless plates (0·78 g), m.p. 225°. (Found: C, 60·2; H, 3·1; N, 11·0. $C_{19}H_{13}O_6N_3$ requires: C, 60·2; H, 3·4; N, 11·1%).

o-(2,4-Dinitrophenoxy)-N-methylbenzanilide

N-Methylsalicylanilide (1·14 g), DNCB (1·14 g) and triethylamine (0·7 ml) were dissolved in DMF (20 ml) and shaken for 24 hr at 25–30°, poured into water (250 ml), and acidified with a few drops of conc HCl. The yellow precipitate crystallized from ethanol in pale yellow plates (0·8 g), m.p. 176°. (Found: C, 16·4; H, 3·7; N, 10·5. $C_{20}H_{15}O_6N_3$ requires: C, 61·1; H, 3·8; N, 10·7%).

Salicyl-2,4-dinitroanilide (I)

A solution of salicylamide (1·4 g) in ethanol (20 ml) and 10% NaOH (4 ml) was stirred with DNCB (2·5 g) at 70–75° for 3 hr. The yellow precipitate obtained on adding water (150 ml) crystallized from benzene in yellow needles (0·78 g), m.p. 213–214° (Tozer and Smiles, m.p. 213°). (Found: C, 51·6; H, 3·2; N, 14·0. Calc. for $C_{13}H_9O_6N_3$: C, 51·5; H, 3·0; N, 13·9%).

Relative rates of reaction of aniline, N-methylsalicylanilide, p-hydroxybenzanilide and salicylanilide with DNCB

(a) Aniline (0·186 g; 0·002 M,) DNCB (0·405 g; 0·002 M) and triethylamine (0·28 ml; 0·002 M) were heated in DMF (10 ml) for 1 hr at 65–66°, poured into water (50 ml), and acidified with conc HCl. The resulting solution was extracted with benzene, and the benzene solution chromatographed on alumina. The reddish yellow band was eluted with benzene and the solvent distilled off. The residue was taken up in ethanol (5 ml) and cooled to 0°. Red needles of 2,4-dinitrodiphenylamine (0·23 g), m.p. 158°, were obtained.

(b) N-Methylsalicylanilide (0·454 g; 0·002 M) was reacted with DNCB under similar conditions. Isolation of the product with ether and crystallization from ethanol by cooling to 0° gave pale yellow plates (0·104 g), m.p. 176°.

(c) *p*-Hydroxybenzanilide (0·852 g; 0·004 M) was condensed with molar proportions of DNCB and triethylamine as above, poured into water (50 ml), and acidified with dilute HNO_3. The precipitate was filtered off, washed with cold ethanol, and dried (0·512 g; m.p. 222°). The aqueous filtrate was extracted with ether and the chloride in the aqueous solution was estimated as AgCl (0·1807 g). The amount of AgCl obtained is somewhat less than that expected from the yield of *o*-dinitrophenyl derivative. Some silver chloride is lost in the course of the analysis due to peptization, perhaps caused by unreacted *p*-hydroxybenzanilide in aqueous solution.

(d) Carrying out the above experiment on salicylanilide (0·852 g), the amount of AgCl was 0·507 g. The N-2,4-dinitrophenyl derivative (0·910 g) was isolated after extraction of the acidified solution with ether and crystallization from ethanol cooled to 0°. The amount of AgCl corresponds to 88% reaction, whereas the N-dinitrophenyl derivative isolated was only 53%. The discrepancy arises partly from the solubility of the dinitrophenyl derivative in ethanol and partly from side reactions, which were indicated by a large number of bands observed when the mother liquor was concentrated, dissolved in benzene and chromatographed on Florex. In experiments (a), (b) and (c) the recovery of the products was nearly quantitative.

Hydrolysis of III

(a) A solution of (III; 0·5 g) in ethanol (5 ml), 10% NaOH (5 ml) and water (40 ml) was stirred at 75–80° for 3 hr. The orange precipitate crystallized from ethanol (Norit) in red needles (0·19 g), m.p. 158°, alone or mixed with 2,4-dinitrodiphenylamine. The filtrate was saturated with carbon dioxide, filtered again, acidified with HCl and cooled. The precipitate, after two crystallizations from aqueous ethanol (Norit) gave brownish plates (0·1 g), m.p. 219°, identified as 2-hydroxy-3-naphthoic acid.

(b) A mixture of III (0·5 g), ethanol (10 ml), water (40 ml) and sodium carbonate (5 g) was refluxed for 14 hr, and the hot solution filtered. The residue (0·23 g) crystallized from ethanol (Norit) in orange-red needles, m.p. 158°, identified as 2,4-dinitrodiphenylamine. From the aqueous filtrate 2-hydroxy-3-naphthoic acid (0·12 g) was recovered.

Naphtol AS RS

The Naphtol, after removal of water-soluble material, crystallized from ethanol in pale brown needles, m.p. 206°. (Found: C, 66·9; H, 4·9; Cl, 10·8; N, 4·4. $C_{17}H_{14}O_3ClN$ requires: C, 66·8; H, 4·7; Cl, 10·4; N, 4·1%). An alcoholic solution gives an olive-green colour with ferric chloride. The dye obtained by coupling with diazotized aniline crystallized from glacial acetic acid in red needles, m.p. 268°. (Found: C, 67·7; H, 4·7; Cl, 8·1; N, 9·4. $C_{23}H_{18}O_3ClN_3$ requires: C, 67·3; H, 4·5; Cl, 8·0; N, 9·4%).

N-(2,4-*Dinitrophenyl*)-*Naphtol* AS-RS

Naphtol AS RS (1·7 g) and DNCB (1·1 g) were dissolved in triethylamine (0·75 ml) and DMF (25 ml) and shaken at 25° for 24 hr. Dilution with water (250 ml) gave a precipitate which crystallized

from benzene-hexane (Norit) in yellow plates (1·8 g). Recrystallization from ethanol gave yellow cubes, m.p. 199°. (Found: C, 59·4; H, 3·0; Cl, 6·5; N, 8·2; OMe, 6·2. $C_{23}H_{16}O_7ClN_3$ requires: C, 59·2; H, 3·5; Cl, 7·0; N, 8·3; OMe, 6·1%).

Hydrolysis of the DNP *derivative of Naphtol* AS-RS

(a) The derivative (0·5 g) was hydrolysed with aqueous NaOH as in the case of III. The acid (0·09 g) melted at 219°, gave a greenish blue colour with alcoholic ferric chloride, and did not depress the m.p. of 2-hydroxy-3-naphthoic acid. The alkali-insoluble orange compound (0·28 g) crystallized from benzene–hexane in red needles, m.p. 201°. (Found: C, 49·7; H, 3·3; Cl, 10·3; N, 12·5; OMe, 9·1. $C_{14}H_{12}O_5ClN_3$ requires: C, 50·0; H, 3·6; Cl, 10·5; N, 12·4; OMe, 9·2%).

Condensation of 6-chlorocresidine with DNCB

A solution of 6-chlorocresidine (0·54 g), DNCB (0·7 g) and triethylamine (0·5 ml) in DMF (5 ml) was shaken at 25° for 24 hr and then poured into water (100 ml). The red precipitate crystallized from benzene (Norit) in red needles (0·38 g), m.p. 201°, not depressed by mixing with the alkali-insoluble product of the hydrolysis of the DNP derivative of Naphtol AS RS.

Condensation product (VII) *of 6-chlorocresidine with 2-hydroxy-3-naphthoyl chloride*

2-Hydroxy-3-naphthoyl chloride (0·3 g) and 6-chlorocresidine (0·2 g) were refluxed in pyridine (5 ml) for 3 hr and then poured into dilute HCl. The precipitate was filtered, washed with water and sodium bicarbonate solution, dried and crystallized from benzene (Norit). The yellow plates (0·22 g), m.p. 206°, did not depress the m.p. of Naphtol AS-RS.

Naphtol AS-KN

The Naphtol, thrice crystallized from DMF, was obtained as pale brown plates m.p. 304°. (Found: C, 78·3; H, 4.5; N, 4·0. $C_{23}H_{16}O_3N$ requires: C, 78·2; H, 4·2; N, 4·0%).

N-(2,4-*Dinitrophenyl*)-*Naphtol* AS KN

Naphtol AS KN (1·75 g), DNCB (1·1 g), triethylamine (0·75 ml) and DMF (25 ml) were shaken for 24 hr at 25°. The product (2·35 g), crystallized successively from benzene–hexane and chlorobenzene–petroleum ether (b.p. 110–120°), was obtained as yellow prisms, m.p. 170°. (Found: C, 67·0; H, 3·0; N, 7·6. $C_{29}H_{17}O_7N_3$ requires: C, 67·0; H, 3·3; N, 8·1%).

Hydrolysis of the DNP *derivative of Naphtol* AS-KN

The compound (1 g) was refluxed for 4 hr with ethanol (10 ml), 10% NaOH (10 ml) and water (80 ml). The alkali-insoluble product was taken up in benzene and chromatographed on alumina. The golden yellow band was eluted with benzene, concentrated, and diluted with a little hexane. Orange-red needles (0·26 g), m.p. 192°, were obtained. (Found: C, 61·8; H, 3·8; N, 13·7. Calc. for $C_{16}H_{11}O_4N_3$: C, 62·1; H, 3·6; N, 13·6%). This did not depress the m.p. of N-(2,4-dinitrophenyl)-α-naphthylamine. The alkaline filtrate obtained from the hydrolysis was saturated with carbon dioxide, filtered, acidified and extracted with ether. The ether extract yielded an acid (0·14 g), which crystallized from ethanol (Norit) in colourless needles, m.p. 293° (decomp). (Found: C, 68·5; H, 3·7. Calc. for $C_{13}H_8O_4$: C, 68·4; H, 3·5%). The alcoholic solution gives a reddish blue ferric colour.

N-(2,4-*Dinitrophenyl*)-*Naphtol* AS BT

Naphtol AS-BT (1·8 g) was treated with DNCB (1·1 g), triethylamine (0·8 ml) and DMF (25 ml) under the usual conditions. The product crystallized from ethanol in yellow rods (1·74 g); crystallization from chlorobenzene-petroleum ether (b.p. 110–120°) gave yellow prisms, m.p. 137°. (Found: C, 61·8; H, 3·8; N, 7·4. $C_{27}H_{18}O_9N_3$ requires: C, 61·3; H, 3·6; N, 7·9%).

Hydrolysis of the DNP *derivative of Naphtol* AS BT

The compound (2 g) was heated with ethanol (20 ml), 10% NaOH (20 ml) and water (160 ml) for 8 hr. The orange precipitate was filtered, and from the filtrate the acid was recovered as usual. It crystallized from ethanol in needles (0·24 g), m.p. 293° (decomp), not depressed by mixing with the acid component of Naphtol AS KN. The alkali-insoluble orange product, after chromatography of

a chlorobenzene solution on alumina, crystallized from benzene in red needles (0·49 g), m.p. 188°. (Found: C, 52·8; H, 3·8; N, 12·9. $C_{14}H_{13}O_6N_3$ requires: C, 52·7; H, 4·1; N, 13·2%). The substance was identified as 2,4-dinitro-2′,5′-dimethoxydiphenylamine, prepared by condensing DNCB with 2,5-dimethoxyaniline.

Condensation of 3-hydroxydibenzofuran-2-carboxylic acid with α-naphthylamine

The acid (0·22 g) in chlorobenzene (20 ml) and DMF (1 ml) was heated on a water-bath with thionyl chloride (0·8 ml) for 15 min. To the clear solution α-naphthylamine (0·14 g) in chlorobenzene (10 ml) and pyridine (2 ml) was added, and heating continued for 45 min. Chlorobenzene was steam-distilled, and the residue washed with sodium carbonate solution and a little methanol. Crystallization from cellosolve gave plates, m.p. 304°, not depressed by mixing with Naphtol AS KN (DRP 607,381 quotes m.p. of 295° for this compound).

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