

The Interaction between Halogen Acids and Nitro-amines

IV*. The Reactivity of Some Nitronaphthylamines

L. SIHLBOM

Institute of Organic Chemistry and Biochemistry, University of Stockholm, Sweden

The reaction between hydrochloric acid and some mononuclear-substituted mono- and dinitronaphthylamines has been investigated and discussed. When treated with hydrochloric acid, 2-nitro-1-naphthylamine and 1-nitro-2-naphthylamine are converted to diazonium salts while 3-nitro-2-naphthylamine remains unchanged. The *m*-nitronaphthylamines and *p*-nitronaphthylamine do not react. All three dinitro-1-naphthylamines were investigated and found to give diazonium salts.

3,4-Dinitro-1-naphthylamine was also subjected to the action of hydrobromic acid. Diazonium salts are formed but other reactions simultaneously take place. The reaction products which were isolated indicate the formation of a brominating agent obviously originating from the reaction between hydrobromic acid and the displaced nitro-group.

In connexion with this investigation 2,3- and 3,4-dinitro-1-naphthylamine have been prepared.

The present part of this series deals with the reaction between hydrochloric acid and some mononuclear-substituted mono- and dinitronaphthylamines. 3,4-Dinitro-1-naphthylamine, the most reactive of the investigated amines, was also reacted with hydrobromic acid.

PREPARATION OF THE NITRONAPHTHYLAMINES

With the exception of 2,3- and 3,4-dinitro-1-naphthylamine the compounds investigated were prepared according to methods reported in the literature.

Hodgson and Turner¹ claimed to have prepared 2,3-dinitro-1-naphthylamine by nitration of 3-nitro-1-acetnaphthalide and subsequent hydrolysis of the resulting 2,3-dinitro-1-acetnaphthalide. Several authors²⁻⁵ seem to have been able to repeat these experiments. The present author has been unable to

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do this. Ward and Coulson⁶ reinvestigated the nitration under the conditions used by Hodgson and Turner and obtained a reaction product consisting of a mixture of 3,5- and 3,8-dinitro-1-acetnaphthalide.

In the present investigation the nitration of 3-nitro-1-acetnaphthalide was carried out in glacial acetic in the presence of boron trifluoride giving in good yield a mixture of 2,3- and 3,4-dinitro-1-acetnaphthalide (ratio *ca.* 1:4). The isomers were separated by taking advantage of their different rates of deacylation to the corresponding amines. Owing to the mobility of the 4-nitro-group, special methods must be used for the deacylation of 3,4-dinitro-1-acetnaphthalide. Two useful methods were found, namely heating its solution in alcohol either with sodium alcoholate⁷ or with boron trifluoride⁸.

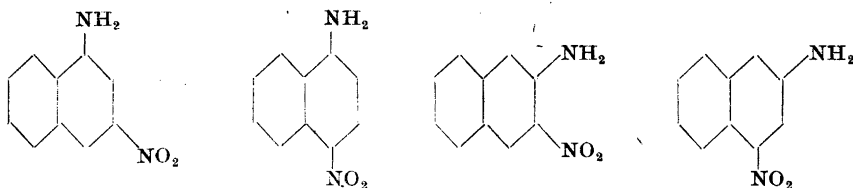
To establish the structures of the amines they were oxidized with aqueous potassium permanganate. Both isomers yielded *o*-phthalic acid which proves that they are mononuclear-substituted derivatives of naphthalene and, consequently, the structures must be 2,3- and 3,4-dinitro-1-naphthylamine. These structures were suggested already by the fact that both amines, when treated with hydrochloric acid, replace one nitro-group by chlorine with formation of diazonium salts (*cf.* below). Hitherto this reaction has been observed only for amines having a nitro-group in the *ortho* or *para* position relative to the amino-group. The structure 3,4-dinitro-1-naphthylamine is ascribed to the amine which, when treated with hydrochloric acid, yields 4-chloro-3-chloronitronaphthalene-1-diazonium chloride.

Hodgson and Turner¹ reported, for 2,3-dinitro-1-acetnaphthalide, a m.p. of 275°. The same compound (m.p. 275.5°) was obtained by Hodgson and Elliott⁹ by nitration of 3-chloro-1-acetnaphthalide with nitric acid. The 2,3-dinitro-1-acetnaphthalide obtained in the present investigation melted at *ca.* 254° (decomp.) and according to a determination of the mixed melting point carried out by Ward¹⁰ it is definitively not identical with the 2,3-dinitro-1-acetnaphthalide prepared by Hodgson and Elliott. Moreover, the corresponding amines also differ considerably. That prepared by Hodgson and Turner melted at 160–61° while that obtained by the author melted at *ca.* 233° (decomp.).

It may be mentioned that 3,4-dinitro-1-naphthylamine (but not 2,3-dinitro-1-naphthylamine) shows chromo-isomerism. Crystals separating from hot toluene or xylene solutions are orange-yellow while those from cold solutions are bright red. When heated to about 190° the red form turns orange-yellow and this colour persists on cooling.

THE REACTION BETWEEN HYDROCHLORIC ACID AND THE NITRONAPHTHYLAMINES

In the investigation of the reactivity of the nitronaphthylamines, the methods described in the previous part of this series¹¹ were used (*cf.* also the experimental part of the present paper). Of the amines investigated, the following remain unchanged when kept for two hours at 100° in a mixture of glacial acetic and hydrochloric acids:



The amines which give diazonium salts on similar treatment are listed in Table 1. A rough idea of the reactivity of the nitro-amines is obtained from the curves in Figs. 1—2, where the amounts of diazonium salts present in the reaction solution are plotted against the time of reaction. Only 1-nitro-2-naphthylamine and 3,4-dinitro-1-naphthylamine are reactive enough to give diazonium salts at 40° (Fig. 1); the others require a higher temperature and were, therefore, reacted at 80° (Fig. 2). Owing to the relatively low solubility of some of the nitronaphthylamine hydrochlorides the experiments had to be carried out in solutions which were more dilute than those used for the dinitro anilines. For comparison 3,4-dinitroaniline was reacted at the concentrations used for the nitronaphthylamines and the corresponding curves are shown in Figs. 1—2.

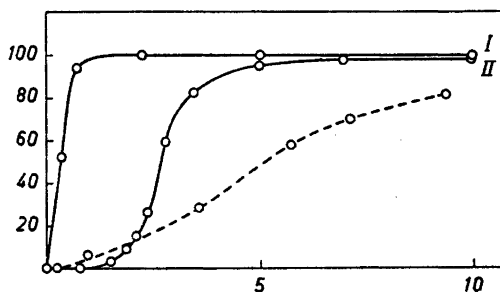


Fig. 1. Relation between yields of diazonium salts in per cent of the theoretical (ordinate) and time of reaction in hours (abscissa). Reaction temperature 40° C. I. 3,4-Dinitro-1-naphthylamine. II. 1-Nitro-2-naphthylamine. --- 3,4-Dinitroaniline.

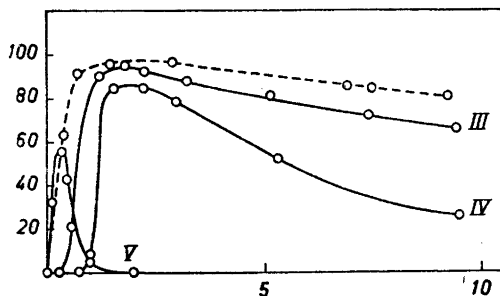
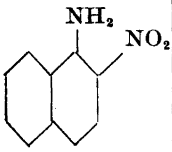
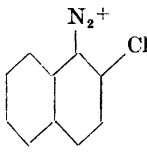
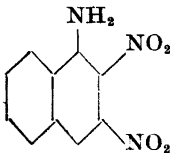
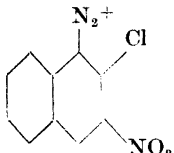
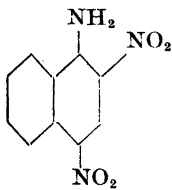
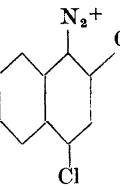
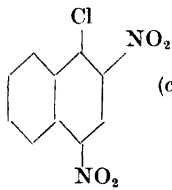
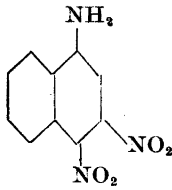
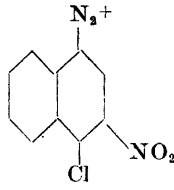
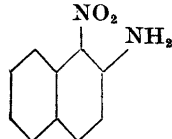
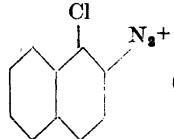


Fig. 2. Coordinates the same as in Fig. 1. Reaction temperature 80° C. III. 2-Nitro-1-naphthylamine. IV. 2,4-Dinitro-1-naphthylamine. V. 2,3-Dinitro-1-naphthylamine. --- 3,4-Dinitroaniline.

Table 1. Compounds obtained from the nitronaphthylamines which on treatment with hydrochloric acid give diazonium salts.

Nitronaphthyl-amine	Temp. °C	Time min.	Reaction products
	80	100	 (ca. 95 %) *
	80	25	 (ca. 55 %)
	80	120	 (ca. 85 %);  (ca. 2 %)
	40	60	 (ca. 100 %)
	40	360	 (ca. 100 %)

* The yields of diazonium salts correspond to the maxima of the curves in Figs. 1-2.

The products formed from the reactive nitronaphthylamines are listed in Table 1. The methods used for identification of the products appear from the experimental section but some comments will be given here.

In the cases of 2-chloro-, 2,4-dichloro- and 4-chloro-3-nitronaphthalene-1-diazonium chloride, the diazonium group was replaced by hydrogen by reduction with hypophosphorous acid; 1-chloronaphthalene-2-diazonium chloride was converted to 1-chloro-2-iodonaphthalene with potassium iodide. The

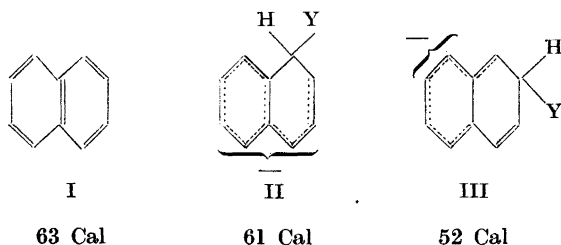
compounds were identified by determination of the mixed melting points with authentic samples. The diazonium salt formed from 2,3-dinitro-1-naphthylamine decomposes rapidly at the reaction temperature (80°) and its structure was, therefore, determined in a different way. When after three hours the presence of diazonium salt could no longer be detected the solution was worked up and a chloronitronaphthol and a small amount of the starting material were isolated. The naphthol was characterized by its methyl ether but the structure has not been rigorously proved. However, in view of the fact that, by the reaction between hydrochloric acid and nitro-amines, only nitro-groups *ortho* or *para* to the amino-group have hitherto been found to be replaced by chlorine and that, in all cases investigated, the chlorine enters the position vacated by the nitro-group, the structure of this naphthol is most probably 2-chloro-3-nitro-1-naphthol.

The chain mechanism postulated for the other nitro-amines investigated¹¹⁻¹² is assumed to operate also in the case of the nitronaphthylamines.

The investigation has shown that some of the nitronaphthylamines are more reactive than the corresponding derivatives of aniline. Thus 2-nitro-1-naphthylamine and 1-nitro-2-naphthylamine react smoothly at 80° and 40°, respectively, whereas *o*-nitroaniline fails to react even at 100°. Further, 3,4-dinitro-1-naphthylamine is more reactive than 3,4-dinitroaniline. 3-Nitro-2-naphthylamine and 4-nitro-1-naphthylamine resemble *o*- and *p*-nitroaniline in remaining unchanged at 100°. 2,3-Dinitro-1-naphthylamine is less reactive than 2,3-dinitroaniline which reacts rather rapidly even at 40° (*cf.* part III¹¹).

The relatively high reactivity of the 1,2-derivatives may be attributed to the greater multiplicity of a 1,2-bond of naphthalene as compared with that of a 2,3-bond (the multiplicities given by Coulson, Daudel and Robertson¹³ are 1.725 and 1.603, respectively). This property of a 1,2-bond may also be responsible for the apparently great effect exerted by the 3-nitro-group in the case of 3,4-dinitro-1-naphthylamine. On the other hand, the relatively small multiplicity of the 2,3-bond may contribute to the nonreactivity of 3-nitro-2-naphthylamine and to the comparatively low reactivity of 2,3-dinitro-1-naphthylamine.

The different reactivities of the 1,2-derivatives indicate that a nitro-group in the 1-position is more easily replaced than one in the 2-position. This was to be expected from the theory presented by Dewar¹⁴. He has discussed the nucleophilic substitution in naphthalene and from the differences in the resonance energies of the parent compound (I) and the transition states (II, III) he concludes that substitution should take place more readily in the 1-position.



It should be pointed out that the velocity of diazonium salt formation is not only dependent on the replaceability of the nitro-group but also on other factors (*cf.* part III¹¹). For instance, the rate of decomposition of the diazonium salt always is of importance and, as in the case of 2,3-dinitro-1-naphthylamine, the reaction products can apparently retard the process. This amine gave diazonium salt in a yield of about 55 % within 20 minutes but nevertheless small amounts of the starting material could be isolated from the reaction solution even after three hours. From this it is obvious that only an approximate comparison of the ease of replaceability of the nitro-groups may be made on the basis of the curves in Figs. 1—2.

THE REACTION BETWEEN HYDROBROMIC ACID AND 3,4-DINITRO-1-NAPHTHYLAMINE

In the replacement experiments already mentioned, hydrochloric acid was employed. In the case of 3,4-dinitro-1-naphthylamine, the most reactive of the investigated amines, the reaction with hydrobromic acid was also studied. In an experiment carried out at 80°, the presence of diazonium salt could be demonstrated even after three minutes. Large amounts of diazonium salts, however, were never present in the solution, and after three hours none could be detected. After another two hours the solution was worked up. By chromatography (Al_2O_3 , benzene), fractions accounting for about 45 % of the adsorbed amount of the reaction product were isolated. The product obtained by elution of the first zone, (about 26 % of the adsorbed amount), yielded by repeated chromatography (Al_2O_3 , light petroleum) three fractions, the analyses of which suggested that the main products were mono-, di- and tribromonitronaphthalene, respectively. The results are displayed in Table 2. Each fraction is named from the compound which may be the main component. The yields which are given in per cent of the total amount of the reaction product adsorbed are rather approximate.

Table 2. Compounds formed in the reaction between hydrobromic acid and 3,4-dinitro-1-naphthylamine

Fraction	M. p. °C	Yield %
Tribromonitronaphthalene	208—11	3
Dibromonitronaphthalene	115—45	8
Monobromonitronaphthalene	78—85	6
Dibromonitronaphthylamine	165—68	4
Monobromodinitronaphthylamine	239—40 (decomp.)	11
3,4-Dinitro-1-naphthylamine	199 (decomp.)	2

As indicated by the analyses and the melting points, the fractions, with the exception of 3,4-dinitro-1-naphthylamine and probably also of monobromodinitronaphthylamine, consisted of more than one compound. Nevertheless, the results give some information about the reaction.

The presence of tribromonitronaphthalene, dibromonitronaphthylamine and monobromodinitronaphthylamine indicates the formation of a brominating agent, obviously originating from the reaction between hydrobromic acid and the displaced nitro-group. This consumption of the diazotising agent inhibits the formation of the 3,4-dinitronaphthalene-1-diazonium ion which is an intermediate of importance for the total rate of the process. Therefore, the rate should be lower when hydrobromic acid is used and as a matter of fact some starting material could be recovered even after five hours (80°). For comparison, 3,4-dinitro-1-naphthylamine, when treated with hydrochloric acid at 40°, was quantitatively converted to 4-chloro-3-nitronaphthalene-1-diazonium chloride in about one hour.

The reaction mechanism outlined here is the same as that postulated for the reaction between hydrobromic acid and 2,3-dinitroaniline (cf. part III¹¹). However, bromoderivatives indicating the formation of a brominating agent could not be isolated in that case.

The formation of a monobromonitronaphthalene is remarkable. This means that one of the nitro-groups or the amino-group has been replaced by hydrogen. For comparison, it may be mentioned that, on treatment with hydrochloric acid in the presence of *p*-chloroaniline, 4,9-dinitro-3-aminoretene is partly converted to 9-nitro-3-aminoretene¹².

As mentioned above the chromatographically isolated products accounted for only about 45 % of the reaction product. The remaining 55 %, occurring in several dark zones in the top of the column, was not further investigated.

EXPERIMENTAL *

Preparation of the nitronaphthylamines

The syntheses of 2- and 4-nitro-1-naphthylamine followed the method of Hodgson and Walker¹⁶ and the compounds were purified by two crystallizations from xylene, followed by chromatography (Al₂O₃, benzene). 2-Nitro-1-naphthylamine melted at 144–45° and 4-nitro-1-naphthylamine at 196–97°.

3-Nitro-1-naphthylamine and 4-nitro-2-naphthylamine were prepared by partial reduction of 1,3-dinitronaphthalene as described by Hodgson and Birtwell¹⁶. The amines were crystallized twice from 80 % ethanol and melted at 136–37° and 99–100°, respectively.

1-Nitro-2-naphthylamine. 1-Nitro-2-acetnaphthalide, prepared by the method reported in Org. Syntheses¹⁷, was hydrolyzed as described by Schiemann and Ley¹⁸. The amine so obtained melted at 127–28.5°.

3-Nitro-2-naphthylamine. Verkade *et al.*, the first to prepare this compound, and Ward (cf. Ref.¹⁹) kindly placed samples at my disposal.

2,4-Dinitro-1-naphthylamine was prepared by the improved method presented by Hodgson and Birtwell²⁰. After two crystallizations from glacial acetic acid it melted at 244–45°.

2,3-Dinitro-1-naphthylamine and 3,4-dinitro-1-naphthylamine. 3-Nitro-1-acetnaphthalide (6.90 g, 0.03 mole) was suspended in glacial acetic acid (90 ml) containing boron trifluoride (9.0 g). A mixture of nitric acid (3.20 g, 0.05 mole, *d* 1.5), glacial acetic acid (30 ml), and boron trifluoride (3.0 g) was added and, while stirring, the suspension was heated to 65–70°. A clear solution was obtained in 10–15 minutes (in some experiments, where the nitration did not start at this temperature, a crystal of sodium nitrite was added). After 5 minutes the solution was cooled and poured into water (1 000 ml). The yellow precipitate formed (6.60 g) was collected, washed with water, dried and crystal-

* All melting points are corrected.

lized from glacial acetic acid (110 ml) giving a yellow well-crystalline product (5.70 g), m. p. ca. 235° (decomp.). The product was dissolved in hot glacial acetic acid (200 ml), the solution allowed to cool to 45–50° and the crystals which separated collected. After another crystallization from glacial acetic acid (85 ml), pure 3,4-dinitro-1-acetnaphthalide (1.60 g), m. p. ca. 263° (decomp.), was obtained as yellow needles. (Found: N 15.0. Calc. for $C_{12}H_9O_5N_3$ (275.2): N 15.3).

The combined filtrates were diluted with water, most of the acid neutralized, and the yellow precipitate formed (3.85 g) collected, washed with water, dried, and refluxed 40 minutes with methanol (115 ml) containing boron trifluoride (11.5 g) to deacylate 3,4-dinitro-1-acetnaphthalide. The red solution so obtained was diluted with water and the precipitated yellow product collected, washed with water, dried, and finely suspended in ether (700 ml). The suspension was refluxed and the insoluble product consisting of almost pure 2,3-dinitro-1-acetnaphthalide (1.40 g), m. p. ca. 250° (decomp.) was crystallized from glacial acetic acid (25 ml) giving light yellow needles (1.20 g), m. p. ca. 254° (decomp.). (Found: N 15.3. Calc. for $C_{12}H_9O_5N_3$ (275.2): N 15.3).

The residue obtained on evaporation of the ether consisted of 3,4-dinitro-1-naphthylamine (2.00 g), m. p. 185–87° (decomp.), which, after one crystallization from glacial acetic acid (25 ml), was obtained as reddish-brown flat needles (1.20 g), m. p. ca. 202° (decomp.) (the solubility of 3,4-dinitro-1-naphthylamine in ether is about 3 g/l). A sample was crystallized twice from *n*-propanol (charcoal) and formed orange-yellow needles, m. p. ca. 205° (decomp.). (Found: C 51.6; H 2.85; N 17.8. Calc. for $C_{10}H_7O_4N_3$ (233.2): C 51.5; H 3.03; N 18.0). From rapidly chilled toluene or xylene solutions, the amine was obtained in the form of bright red crystals. From hot solutions the orange-yellow form separated.

2,3-Dinitro-1-acetnaphthalide was hydrolyzed by dissolving the compound (1.0 g) in ethanol (80 ml), adding 50 % sulphuric acid (80 ml) and refluxing the solution for 3 hours. After dilution of the solution with water the precipitated 2,3-dinitro-1-naphthylamine (0.80 g), m. p. 225–227° (decomp.), was collected, washed with water, dried and crystallized from *n*-propanol (40 ml) giving yellow needles (0.62 g), m. p. ca. 233° (decomp.). (Found: C 51.3; H 2.99; N 18.2. Calc. for $C_{10}H_7O_4N_3$ (233.2): C 51.5; H 3.03; N 18.0).

3,4-Dinitro-1-acetnaphthalide was deacylated by refluxing the compound in methanol containing boron trifluoride, as described by Sihlbom⁸.

The oxidation of the two amines for establishing the orientation of the nitro-groups was carried out in the following way (cf. Hodgson and Hathway²¹). A mixture of finely powdered dinitronaphthylamine (0.15 g), potassium permanganate (0.7 g) and water (10 ml) was refluxed for 5 hours. It was worked up as described by Hodgson and Hathway and yielded colourless crystals (0.04 g), m. p. 199°, undepressed on admixture with *o*-phthalic acid.

The structure 3,4-dinitro-1-naphthylamine was ascribed to the amine which, when treated with hydrochloric acid, yielded 4-chloro-3-nitronaphthalene-1-diazonium chloride (cf. below).

The reaction between hydrochloric acid and the nitronaphthylamines

Samples (0.10 g) of 3- and 4-nitro-1-naphthylamine and of 4-nitro-2-naphthylamine in a mixture of glacial acetic acid (10 ml) and hydrochloric acid (2 ml, *d* 1.19) were heated to 100° for 2 hours in sealed tubes. The reaction mixtures were diluted with water, neutralized and the precipitated product collected, washed with water and dried. In each case only the starting material was obtained.

3-Nitro-2-naphthylamine (20 mg) was treated as described above. The acids were evaporated and the almost colourless needles obtained dissolved in ethanol. After the addition of some drops of ammonia and dilution with water a red crystalline product (17 mg) containing no chlorine separated. It melted at 114–15°, undepressed on admixture with 3-nitro-2-naphthylamine.

When treated with hydrochloric acid in glacial acetic acid solution, 2-nitro-1-naphthylamine, 1-nitro-2-naphthylamine, 2,4- and 3,4-dinitro-1-naphthylamine were quantitatively consumed and diazonium salts were formed. Similarly, 2,3-dinitro-1-naphthylamine gave

a diazonium salt; the reaction was rapid in the beginning but soon slowed down. Even after 3 hours, unchanged dinitronaphthylamine was present in the solution.

The rate of diazonium salt formation was determined as described in the preceding paper of this series ¹¹. The amine (0.003 mole; in the case of the slightly less soluble 3,4-dinitro-1-naphthylamine 0.002 mole) was dissolved in glacial acetic acid (84 ml) and 12 M hydrochloric acid (17 ml) was added. The reaction solution was kept in a well closed flask. At suitable intervals samples were taken out and the amount of diazonium salt formed determined. 1-Nitro-2-naphthylamine and 3,4-dinitro-1-naphthylamine were allowed to react at $40^{\circ} \pm 0.2^{\circ}$. In the cases of 2-nitro-, 2,3- and 2,4-dinitro-1-naphthylamine, no diazonium salt was formed at this temperature and the reaction was, therefore, carried out at $80^{\circ} \pm 0.2^{\circ}$. In the curves in Figs. 1–2, the yields of diazonium salts are plotted against time of reaction.

The products formed when the reactive nitronaphthylamines were treated with hydrochloric acid were identified in the following way.

2-Nitro-1-naphthylamine (0.003 mole) was dissolved in glacial acetic acid (84 ml) and the solution was mixed with conc. hydrochloric acid (17 ml) and heated in a sealed flask for 2 hours. The reaction solution was then diluted with water (400 ml), extracted with ether to remove a small amount of impurities originating from that fraction of the diazonium salt which had already decomposed, mixed with 50 % hypophosphorous acid (25 ml), kept at $5-10^{\circ}$ overnight and again extracted with ether. The latter ether solution was washed with aqueous sodium hydroxide and water, dried over Na_2SO_4 and decolourized with a little charcoal. Evaporation of the ether yielded almost colourless crystals (0.35 g, 72 %), m. p. $49-51^{\circ}$, which were crystallized from light petroleum giving leaflets, m. p. $55-56^{\circ}$, undepressed on admixture with 2-chloronaphthalene.

1-Nitro-2-naphthylamine (0.005 mole) was dissolved in glacial acetic acid (84 ml), conc. hydrochloric acid (17 ml) was added and the solution kept at 40° for 10 hours. A saturated aqueous potassium iodide solution (50 ml) was added while stirring, causing rapid decomposition of the diazonium salt. After 3 hours, water (100 ml) was added and the product precipitated was collected, washed with water, dried, and extracted with ligroin. On evaporation of the solvent a crystalline substance (1.10 g), m. p. $73-76^{\circ}$, was obtained. One crystallization from ethanol (10 ml) gave light orange-yellow needles (0.65 g, 45 %), m. p. $82-83.5^{\circ}$, undepressed on admixture with 1-chloro-2-iodonaphthalene.

2,3-Dinitro-1-naphthylamine (0.001 mole) was dissolved in glacial acetic acid (30 ml), conc. hydrochloric acid (6 ml) added and the solution kept in a closed flask at 80° for 3 hours. After dilution with water most of the acids were neutralized and the separated product (0.17 g) was collected, washed with water and dried. The product was dissolved in ether and the solution saturated with ammonia. The red precipitate formed was collected and suspended in ether. The introduction of hydrogen chloride yielded a yellow solution; the ammonium chloride was removed and the ether evaporated. An orange coloured crystalline residue (65 mg, 29 %), m. p. $154-55^{\circ}$, consisting of 2-chloro-3-nitro-1-naphthol was obtained. From ligroin-benzene it separated as orange coloured needles. (Found: C 53.6; H 2.69; N 6.40; Cl 16.0. Calc. for $\text{C}_{10}\text{H}_6\text{O}_2\text{NCl}$ (233.6): C 53.8; H 2.59; N 6.27; Cl 15.9).

The methyl ether. 2-Chloro-3-nitro-1-naphthol (25 mg) was dissolved in ether (15 ml) containing excess of diazomethane and the solution was kept overnight. Evaporation of the ether yielded a light-yellow product (25 mg), m. p. $75-77^{\circ}$. After one crystallization from ethanol light-yellow needles, m. p. $86-87^{\circ}$ were obtained. (Found: C 55.6; H 3.57. Calc. for $\text{C}_{11}\text{H}_8\text{O}_2\text{NCl}$ (237.6): C 55.6; H 3.40).

The above ether solution, from which the ammonium naphtholate had been removed, yielded on evaporation of the ether a product which after one crystallization from benzene gave yellow needles (15 mg), m. p. ca. 228° (decomp.), undepressed on admixture with 2,3-dinitro-1-naphthylamine.

2,4-Dinitro-1-naphthylamine (4.0 g) was dissolved in glacial acetic acid (480 ml), conc. hydrochloric acid (100 ml) was added and the solution kept in a closed flask at 80° for 2 hours. The solution was cooled, diluted with water (2 000 ml), extracted with ether, mixed with 50 % hypophosphorous acid (100 ml), kept at $5-10^{\circ}$ for 10 hours and again extracted with ether. Both ether solutions were washed with aqueous sodium hydroxide and water, dried over Na_2SO_4 and decolourized with a little charcoal. The ether was then evaporated.

The yellow product (0.20 g) from the first ether extract was triturated with light petroleum and crystallized from benzene giving light-yellow crystals (70 mg), m. p. 146–47°, undepressed on admixture with 1-chloro-2,4-dinitronaphthalene.

The second ether extract yielded almost colourless crystals (2.20 g, 65%), m. p. 62–63°, undepressed on admixture with 1,3-dichloronaphthalene.

3,4-Dinitro-1-naphthylamine (0.001 mole) was dissolved in warm glacial acetic acid (42 ml) and conc. hydrochloric acid (8.5 ml) was added. The solution was kept at 40° for 1 hour, then cooled, mixed with 50% hypophosphorous acid (20 ml), kept at room temperature for 2 hours, diluted with water (200 ml) and neutralized. The precipitate formed was collected, washed with water and dried. The product (0.15 g), m. p. 74–75°, was further purified by chromatography (Al_2O_3 , benzene) giving a light-yellow product (0.12 g, 58%), m. p. 80–81°, undepressed on admixture with 1-chloro-2-nitronaphthalene.

The reaction between hydrobromic acid and 3,4-dinitro-1-naphthylamine

3,4-Dinitro-1-naphthylamine (0.004 mole) was dissolved in hot glacial acetic acid (90 ml), 40% hydrobromic acid (18 ml) was added and the solution then kept at 80°. The reaction was followed by coupling tests with 3-retenol. Diazonium salts were detected 2–3 minutes after mixing and were shown to be present in the solution during the next 3 hours. After 5 hours the solution was cooled and diluted with water (700 ml). The precipitate formed was collected, washed with water and dried. The product (0.94 g) was dissolved in benzene (10–20 mg of an insoluble red product containing bromine was removed) and adsorbed on a column of alumina (10 cm² × 25 cm). On development with benzene many zones appeared. Zones Nos. 1–3 were eluted by continuing the addition of benzene. Zones Nos. 4–5 which moved very slowly with benzene were taken out and eluted with a mixture of benzene and ethylacetate. The many dark coloured zones remaining in the top of the column were not investigated.

The first zone, very light yellow, yielded a product (0.25 g, 26% of the adsorbed amount) consisting of at least three compounds. After trituration with warm light petroleum, almost colourless crystals (0.03 g), m. p. 208–11° were obtained. (Found: N 3.60; Br 56.4. Calc. for a *tribromonitronaphthalene*, $\text{C}_{10}\text{H}_4\text{O}_2\text{NBr}_3$ (409.9): N 3.42; Br 58.5).

The light petroleum solution was adsorbed on a column of alumina (3 cm² × 20 cm) which was then washed with light petroleum. Two separate, very light yellow zones were formed and successively eluted. The first eluted zone yielded a yellow-white product (0.08 g) which crystallized as needles from ethanol, m. p. 115–45°. (Found: N 4.15; Br 50.8. Calc. for a *dibromonitronaphthalene*, $\text{C}_{10}\text{H}_5\text{O}_2\text{NBr}_2$ (331.0): N 4.23; Br 48.3). The other zone gave a product (0.06 g), m. p. 78–85° which after crystallization from ethanol was obtained as yellow-white needles, m. p. 79–86°. (Found: N 5.53; Br 31.4. Calc. for a *monobromonitronaphthalene*, $\text{C}_{10}\text{H}_6\text{O}_2\text{NBr}$ (252.1): N 5.55; Br 31.7).

The second zone, yellowish brown, furnished only few mg of substance. It was not further investigated.

The third zone, yellow, yielded an amine (0.04 g), m. p. 165–68° which contained bromine. After one crystallization from ethanol it melted at 181–84°. (Found: C 35.7; H 2.00. Calc. for a *dibromonitronaphthylamine*, $\text{C}_{10}\text{H}_5\text{O}_2\text{N}_2\text{Br}_2$ (346.0): C 34.7; H 1.75).

The fourth zone, orange-yellow, also yielded an amine (0.10 g), m. p. 239–40° (decomp.). One crystallization from ethanol did not change the melting point, the amine being obtained as brown yellowish needles. (Found: N 13.1; Br 25.4. Calc. for a *monobromodinitronaphthylamine*, $\text{C}_{10}\text{H}_6\text{O}_2\text{N}_2\text{Br}$ (312.1): N 13.4; Br 25.6).

The amines isolated from zones Nos. 3–4 were readily diazotised in a mixture of glacial acetic and conc. hydrochloric acids. The diazonium salts apparently were not decomposed by the addition of water; they furnished azodyes with 3-retenol.

The fifth zone, reddish-brown, gave 3,4-dinitro-1-naphthylamine (0.02 g), m. p. ca 199° (decomp.), undepressed on admixture with an authentic sample.

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