The Interaction between Halogen Acids and Nitro-amines

## III *. The Reactivity of Mono- and Dinitroanilines

L. SIHLBOM

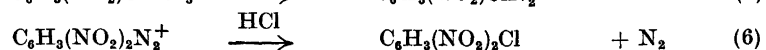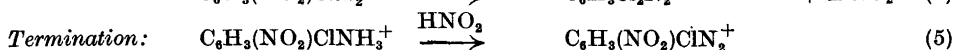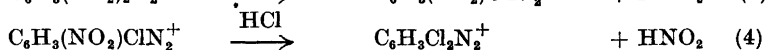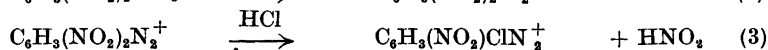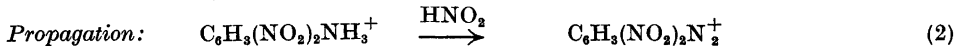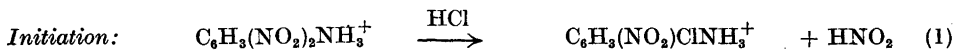*Institute of Organic Chemistry and Biochemistry, University of Stockholm, Sweden*

When treated with hydrochloric acid certain nitro-amines are transformed to chlorosubstituted diazonium salts. This reaction has been described and discussed in the preceding papers of this series [1,2]. The mono- and dinitroanilines have now been studied.

The mononitroanilines failed to yield any diazonium salts when heated to 100 °C in a mixture of glacial acetic and hydrochloric acids and were recovered unchanged.

Of the six dinitroanilines only 3,5-dinitroaniline failed to react; the others reacted quantitatively yielding large amounts of diazonium salts. In order to compare the reactivity of these dinitroanilines they were allowed to react at 40 °C and the amounts of diazonium salts present in the reaction solution were determined at suitable intervals (for 2,4-dinitroaniline a temperature of 80 °C was necessary for the reaction to proceed). The results are shown in Fig. 1 where the amount of diazonium salt is plotted against the time of reaction. The results show that, with regard to reactivity, the dinitroanilines may be arranged in the following order,

$$2,3\text{-} > 3,4\text{-} \geq 2,5\text{-} \quad \text{and} \quad 2,6\text{-} > 2,4\text{-dinitroaniline}.$$
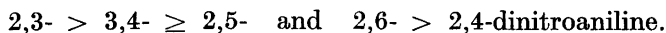
Assuming the chain mechanism postulated for the reaction between 4,9-dinitro-3-aminoretene and hydrochloric acid [2] the formation of the diazonium salts is probably due to the following series of reactions

Initiation:	$C_6H_3(NO_2)_2NH_3^+$ $\xrightarrow{\text{HCl}}$	$C_6H_3(NO_2)ClNH_3^+$	$+ HNO_2$	(1)
Propagation:	$C_6H_3(NO_2)_2NH_3^+$ $\xrightarrow{\text{HNO}_2}$	$C_6H_3(NO_2)_2N_2^+$		(2)
	$C_6H_3(NO_2)_2N_2^+$ $\xrightarrow{\text{HCl}}$	$C_6H_3(NO_2)ClN_2^+$	$+ HNO_2$	(3)
	$C_6H_3(NO_2)ClN_2^+$ $\xrightarrow{\text{HCl}}$	$C_6H_3Cl_2N_2^+$	$+ HNO_2$	(4)
Termination:	$C_6H_3(NO_2)ClNH_3^+$ $\xrightarrow{\text{HNO}_2}$	$C_6H_3(NO_2)ClN_2^+$		(5)
	$C_6H_3(NO_2)_2N_2^+$ $\xrightarrow{\text{HCl}}$	$C_6H_3(NO_2)_2Cl$	$+ N_2$	(6)

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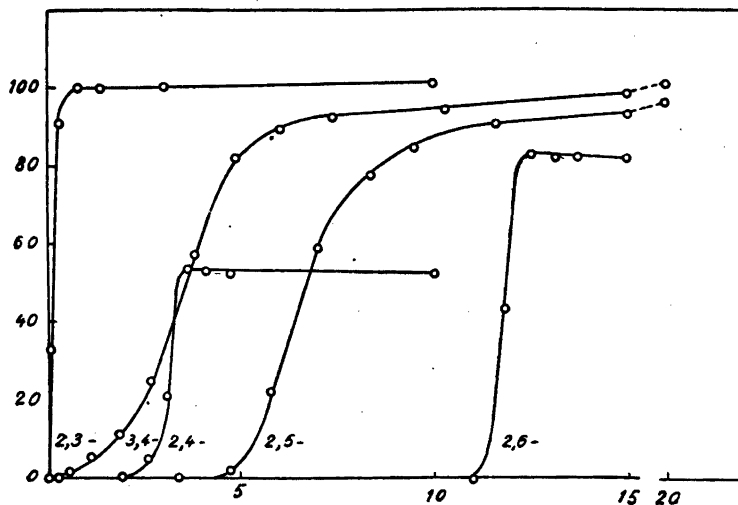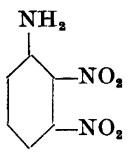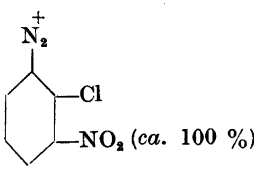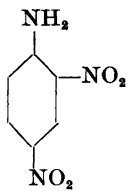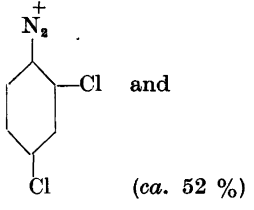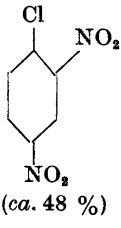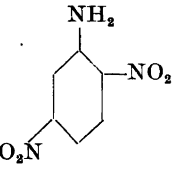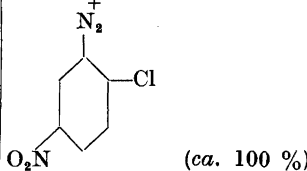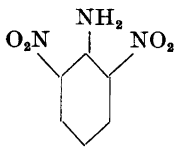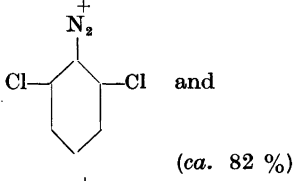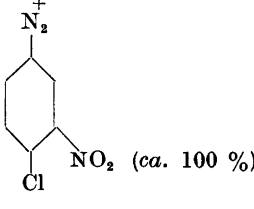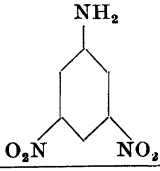
Fig. 1. *Relation between yields of diazonium salts in per cent of the theoretical (ordinate) and time of reaction in hours (abscissa).*

The three most reactive dinitroanilines (2,3-, 2,5-, and 3,4-) gave quantitative yields of the respective chloronitrobenzene diazonium chlorides. These are fairly stable and the second nitrogroup (situated in m-position to the diazonium-group) is not replaced by chlorine. The process takes place *via* reactions (1), (2), (3), and (5). The other isomers (2,4- and 2,6-) are transformed to the relatively stable dichlorobenzene diazonium chlorides and to chlorodinitrobenzenes. It is clear that reactions (4) and (6) also obtain for the latter transformations. The maxima of the curves for the reactions of these two dinitroanilines (see Fig. 1) represent the amounts of dichlorobenzene diazonium chlorides present in the reaction solutions. These dichloro-compounds are formed in yields of more than fifty per cent; thus the amount of nitrous acid produced exceeds that required for the diazotisation of the amino-group and nitric oxide is evolved. The amount of 2,4- and 2,6-dinitrobenzene diazonium chloride which decomposes during the reaction (with formation of chlorodinitrobenzene) has also been determined. For both isomers the sum of stable and unstable diazonium salts accounted for the total amount of the dinitroaniline consumed. The results are listed in Table 1. The methods used for the identification and quantitative determination of the reaction products are given in the experimental section.

The investigation shows that only nitro-groups in o- or p-position to the amino-group are displaced. The different reactivity o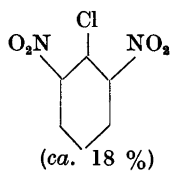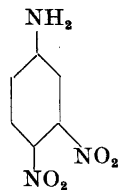f 2,3- and 3,4-dinitroaniline indicates that a nitro-group in o-position to the amino-group is more reactive than one in the p-position. Comparison of the reactivities of 2,3-, 2,4- and 2,5-dinitroaniline shows that the reacting nitro-group is more activated by an adjacent nitro-group than by a p-nitro-group. The latter in turn has a greater influence than a nitro-group in m-position.

Table 1.

Dinitro-aniline	Temp. °C	Time hours	Reaction products
(NH$_2$, 2,3-NO$_2$,NO$_2$ aniline)	40	1	(N$_2^+$, Cl, NO$_2$) *(ca. 100 %)*
(NH$_2$, 2,4-NO$_2$,NO$_2$ aniline)	80	4	(N$_2^+$, 2-Cl, 4-Cl) *(ca. 52 %)* and (Cl, NO$_2$, NO$_2$) *(ca. 48 %)*
(NH$_2$, 2-NO$_2$, 4-O$_2$N aniline)	40	20	(N$_2^+$, Cl, O$_2$N) *(ca. 100 %)*
(O$_2$N, NH$_2$, NO$_2$ aniline)	40	16	(N$_2^+$, Cl, Cl) *(ca. 82 %)* and (O$_2$N, Cl, NO$_2$) *(ca. 18 %)*
(NH$_2$, NO$_2$, NO$_2$ aniline)	40	12	(N$_2^+$, NO$_2$, Cl) *(ca. 100 %)*
(NH$_2$, O$_2$N, NO$_2$ aniline)	100	2	Unchanged material

In agreement with the assumed reaction mechanism, the reaction between dinitroanilines and hydrochloric acid was found to be catalyzed by small amounts of nitrite and retarded by compounds which rapidly consume the diazotising agent formed in the initiating reaction. It was also found that when slightly impure dinitroanilines were used a longer period of time elapsed before detectable amounts of diazonium salts appeared in the solution. However, once started, the diazotisation was generally not influenced by small amounts of impurities. It is probable that the diazotising agent is removed initially by interaction with the impurities and diazotisation of the dinitroaniline does not begin until they are consumed.

To show the velocity of the initiating reaction, the most reactive dinitroaniline (2,3-) was heated to 80 °C for 15 hours with addition of an easily diazotisable amine which rapidly removes the diazotising agent formed. The resulting reaction solution contained no stable diazonium salts and most of the dinitroaniline remained unchanged. Attempts to isolate 2-chloro-3-nitroaniline formed in the initiating reaction failed and, consequently, the initiating reaction must be very slow. By comparison 4,9-dinitro-3-aminoretene reacts quantitatively within 15 minutes under the same conditions [2].

Since the initiating reaction is very slow even for the most reactive dinitroaniline, it may be expected that when a new electron repelling substituent is introduced, no reaction will occur under the preceding conditions. On the other hand, the nitro-groups should be more reactive after the introduction of an electron attracting substituent and as a matter of fact 5-chloro-2,4-dinitroaniline, recently investigated by Dey, Krishna Maller and Pai [3], is more reactive than 2,4-dinitroaniline.

All these experiments were carried out with hydrochloric acid; in the presence of hydrobromic acid the dinitroanilines did not yield detectable amounts of diazonium salts but remained essentially unchanged. Various amounts of hydrobromic acid were used at temperatures varying from 15 to 100 °C and attempts were also made to initiate the reaction by the addition of sodium nitrite. An experiment carried out with 2,3-dinitroaniline at 60 °C showed that on the addition of a very small amount of nitrite (ca. 0.5 % of the theoretical) a chain reaction was started whereby dinitroaniline was converted to 2,3-dibromonitrobenzene. This reaction soon ceased, however, but could be started again with nitrite. After the addition of ten consecutive portions of nitrite (5 % of the theoretical amount) all the dinitroaniline had reacted. Experiments carried out at different temperatures showed that the higher the temperature the larger the amount of nitrite required for complete diazotisation. The termination of the reaction may be due to liberation of bromine by reaction of hydrobromic with nitrous acid. Indeed a mixture of these two acids can be used as a brominating agent. Thus Milton and Reade [4] have used such a mixture for bromination of p-nitrodimethylaniline, and following a method described by them the presence of free bromine could be demonstrated in a mixture of glacial acetic, hydrobromic, and nitrous acids.

Although the reaction between hydrobromic and nitrous acids undoubtedly is partly responsible for the termination, the greater instability of the diazo-

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nium ion in hydrobromic acid solution may also be a factor of importance. Assuming that the initiating reaction is also slow when hydrobromic acid is used, termination will occur though only a small fraction of the dinitrobenzene diazonium ion decomposes before the reactive nitro-group is displaced by bromine. Although no compounds, the presence of which would prove that termination takes place in this way, could be isolated, this possibility can not be excluded. It may be remembered that with hydrochloric acid, 2,4-dinitro-aniline yields 4-chloro-1,3-dinitrobenzene (*ca.* 48 %) and 2,4-dichlorobenzene diazonium chloride (*ca.* 52 %). If more than 50 % of 2,4-dinitrobenzene diazonium chloride were converted to chlorodinitrobenzene, termination should have taken place also in this case.

As mentioned above, 2,3-dinitroaniline is quantitatively diazotised in the presence of hydrobromic acid by an amount of nitrite corresponding to *ca.* 5 % of the theoretical (the reaction product being 2,3-dibromonitrobenzene). If the initiating reaction takes place at all when hydrobromic acid is used, it might be expected that a certain amount of 2,3-dibromonitrobenzene would also be formed when the dinitroaniline is heated with glacial acetic and hydrobromic acids for a long time, in spite of the rapid termination of the expected chain reaction under these conditions. An experiment carried out at 100—110 °C for 15 hours showed that 2,3-dibromonitrobenzene is indeed formed (yield about 15 %), and unchanged dinitroaniline could also be isolated.

Dey *et al.*[3] in an investigation of the reaction between hydrochloric acid and 5-chloro-2,4-dinitroaniline found that this compound "splits off its nitro-groups on merely heating its solution in a mixture of glacial acetic and hydrochloric acids to 100 °C. Nitrous fumes were evolved with effervescence and this was observed to continue even after the heating was discontinued. In the resulting solution the presence of both 1,2,4,5-tetrachlorobenzene and 2,4,5-trichloroaniline were detected. It is therefore seen that mere heating of the compound is enough to eliminate both nitro-groups and replace them by chlorine, thereby giving rise to 2,4,5-trichloroaniline which in its turn is partly diazotised by the nitrous acid originating from the displaced nitro-groups, the resulting diazonium group being replaced by chlorine to yield 1,2,4,5-tetra-chlorobenzene". The assumption that 2,4,5-trichloroaniline should be so easily formed under these conditions is very improbable and it is unlikely that this compound is only partly diazotised when nitrous acid is present in excess. The reaction mechanism postulated for 2,4-dinitroaniline (see p. 1197) seems to be more probable, *i. e.* the reaction takes place *via* 5-chloro-2,4-dinitrobenzene diazonium chloride. Part of the diazonium compound then gives rise to 2,4,5-trichlorobenzene diazonium chloride and another part to 1,5-dichloro-2,4-dinitrobenzene. Repetition of the experiment of Dey *et al.* afforded only these compounds; no trichloroaniline could be detected. Dey *et al.* obtained the latter compound after steam distillation of the reaction solution and treatment of the distillate with tin and hydrochloric acid. It is possible that the trichloro-aniline was formed from 2,4,5-trichloronitrobenzene, although this derivative could not be found in the reaction solution by the present author.

In the first paper of this series [1] it was pointed out that acetic or other carboxylic acids are the only reaction media in which the reaction between halogen acids and nitro-amines takes place. In the case of the dinitroanilines,

however, it was found that the reaction also occurs in an aqueous hydrochloric acid solution. However, the reaction does not proceed as smoothly as in glacial acetic acid solution and 2,4-dinitroaniline remained unchanged even after heating to 100 °C for 15 hours in 2 M hydrochloric acid.

EXPERIMENTAL *

Preparation of the nitroanilines

The *mononitroanilines* were all commercially available in high purity and were not further purified.

2,4-Dinitroaniline. A commercial product was purified by crystallization from ethanol and from glacial acetic acid to m.p. 181—182 °C.

2,6-Dinitroaniline was prepared by the method described in Org. Syntheses [5]. The crude 2,6-dinitroaniline, crystallized twice from ethanol (charcoal), gave m.p. 141—142 °C.

3,5-Dinitroaniline was prepared by reducing 1,3,5-trinitrobenzene with ammonium sulphide by the method of Flürscheim [6]. The crude product was crystallized twice from water (charcoal) to m.p. 162—163 °C.

The syntheses of *2,3-, 2,5-,* and *3,4-dinitroaniline* chiefly followed the method of van de Vliet [7]. In agreement with his description the mixture of the three isomeric dinitro-acetanilides obtained by nitration of m-nitroacetanilide was separated into three fractions (I—III) from which the three dinitroanilines were prepared.

Fraction I consisting of pure 2,3-dinitroacetanilide was hydrolysed with conc. sulphuric acid at 110 °C. On crystallization from benzene pure 2,3-dinitroaniline, m.p. 126—127 °C, was obtained.

Fraction II, which van de Vliet reported to consist of almost pure 3,4-dinitroacetanilide, was hydrolysed as above. A sample of the hydrolysed product was chromatographed (Al₂O₃, benzene) and found to contain 2,3-dinitroaniline (3 %), 2,5-dinitroaniline (17 %), and 3,4-dinitroaniline (72 %). The main part of the hydrolysed product was crystallized from benzene giving pure 3,4-dinitroaniline, m.p. 157—158 °C.

Fraction III reported to be an eutectic mixture of 2,3- and 2,5-dinitroacetanilide was hydrolysed as above. After repeated extraction of the reaction product with hot water van de Vliet obtained a residue (60 %) consisting of rather pure 2,5-dinitroaniline. As only a small amount of material was required for the present investigation, a chromatographic separation (Al₂O₃, benzene) was preferred. In this way pure 2,5-dinitroaniline, m.p. 138—139 °C, was obtained from fraction III in a yield of about 70 %.

The reaction between hydrochloric acid and the mono- and dinitroanilines

o-Nitroaniline (0.50 g) was suspended in a mixture of glacial acetic (10 ml) and conc. hydrochloric acids (2 ml) and heated in a sealed glass tube for 2 hours at 100 °C. After dilution with water and neutralization with sodium carbonate unchanged starting material precipitated and was collected and washed with water. It was obtained in a yield of 0.35 g, m.p. 71—72 °C, undepressed on admixture with o-nitroaniline.

m-Nitroaniline (0.50 g) was treated in the way described above. Unchanged starting material (0.38 g), m.p. 114—115 °C, undepressed on admixture with m-nitroaniline, was obtained.

p-Nitroaniline (0.50 g) was treated in the same way and yielded unchanged starting material (0.41 g), m.p. 150—151 °C, undepressed on admixture with p-nitroaniline.

3,5-Dinitroaniline (0.50 g) was treated as described above, but after neutralization the reaction solution was extracted with ether. The residue (0.50 g, m.p. 143—148 °C) obtained on evaporation of the ether, was suspended in a small volume of ether. The insoluble material (0.03 g) which was collected, had m.p. 184—186 °C, undepressed on
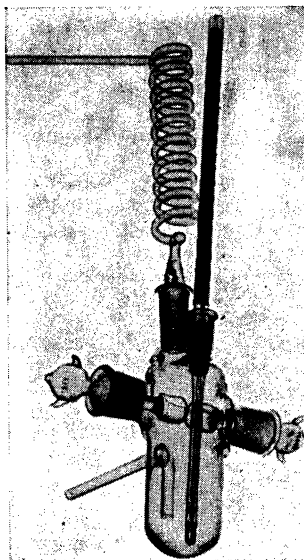
*Fig. 2. Apparatus, used for quantitative
    determination of the diazonium salts.*

admixture with 3,5-dinitroacetanilide. The soluble product melted at 156—157 °C, un-depressed on admixture with 3,5-dinitroaniline.

On treatment with hydrochloric acid *2,3-, 2,4-, 2,5-, 2,6-,* and *3,4-dinitroaniline* were quantitatively consumed and diazonium salts were present in the reaction solution. The following method was used to determine the reactivity of these dinitroanilines.

A sample of the dinitroaniline (1 g) was accurately weighed into a ground-stoppered Erlenmeyer flask and glacial acetic acid (40 ml) added. The flask was placed in a water bath (40 °C ± 0.2 °C) and the clear solution mixed with warm (40 °C) 12 *M* hydrochloric acid (8 ml). In the case of 2,4-dinitroaniline no reaction occurred at 40 °C even after 24 hours. This isomer was therefore allowed to react at 80 °C ± 1 °C whereupon diazonium salts appeared after *ca.* 2 hours. At suitable intervals samples (4 ml) were pipetted into the apparatus used for quantitative determination of the amount of diazonium salt (see Fig. 2). The apparatus was immersed in a water bath at 40° or 80 °C. When the air had been expelled with carbon dioxide, the diazonium salts were decomposed by the addition of cuprous oxide from one of the small containers and the nitrogen evolved was collected in an azotometer containing 50 % aqueous potassium hydroxide. From the amount of nitrogen, the yield of diazonium salts in each sample was calculated. In the curves of Fig. 1 the yields of diazonium salts are plotted against the time of reaction. The first point of each curve indicates the time when the presence of diazonium salts could just be demonstrated (reaction with 3-retenol).

The method described above allows a determination every 15 minutes. In the case of the most reactive isomer, 2,3-dinitroaniline, in order to make a determination after a shorter period of time, the following procedure was used.

A sample of 2,3-dinitroaniline (0.1 g) was weighed into the apparatus and dissolved in glacial acetic acid (4 ml). When the air had been expelled, 12 *M* hydrochloric acid (0.8 ml) was added from the one container and 4 minutes later cuprous oxide was added from the other. The amount of nitrogen was collected in the usual way.

In the investigation of 2,4- and 2,6-dinitroaniline the nitrogen collected in the azotometer was found to contain nitric oxide. In the first experiments the nitric oxide was removed by washing the nitrogen with an alkaline solution of potassium permanganate. However, it was found that the nitric oxide was more conveniently removed if the nitro-

gen (after washing with aqueous sodium carbonate) was passed through a hot (190 °C) tube charged with lead dioxide, before being collected in the azotometer.

The amount of relatively unstable diazonium salt formed when 2,4- and 2,6-dinitroaniline is treated with hydrochloric acid as described above was determined in the following way. As soon as diazonium salts could be detected in the reaction solution an aliquot of this solution was pipetted into the apparatus (Fig. 2) which had been cooled to 5—10 °C to avoid loss of hydrogen chloride while the air was expelled with carbon dioxide. The reaction was then allowed to proceed for 5 hours at the normal reaction temperature. Before entering the azotometer the gases evolved were passed over hot lead dioxide. The amount of diazonium salt which decomposed during the reaction was calculated from the amount of nitrogen collected and was found to be 49 % for 2,4-dinitroaniline and 19 % for 2,6-dinitroaniline.

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

2,3-Dinitroaniline (0.50 g) was dissolved in glacial acetic acid (20 ml) and the solution was mixed with conc. hydrochloric acid (4 ml) and kept at 40 °C. After 1 hour the diazonium salt formed was decomposed by adding the solution to a hot (*ca.* 70 °C) solution of cuprous chloride (4 g) in conc. hydrochloric acid (40 ml). The reaction product was precipitated by addition of water (250 ml), collected, washed with water and dried (yield 0.35 g, 67 %). It melted at 60—61 °C, undepressed on admixture with 2,3-dichloronitrobenzene.

The experiment was repeated in the presence of *p*-chloroaniline. 2,3-Dinitroaniline (0.92 g) and *p*-chloroaniline (1.28 g) were dissolved in glacial acetic acid (40 ml). The solution was mixed with conc. hydrochloric acid (8 ml) and heated to 80 °C for 15 hours. The reaction solution was diluted with water, neutralized with sodium carbonate solution and extracted with ether. The ether solution was washed with water and dried. *p*-Chloroaniline was precipitated as its hydrochloride by the introduction of hydrogen chloride. The ether solution was washed free from hydrogen chloride and the ether evaporated. The residue was crystallized from water (200 ml) yielding yellow crystals (0.70 g), m.p. 126—127 °C, undepressed on admixture with 2,3-dinitroaniline. The mother liquor was extracted with ether yielding a crystalline product (0.10 g) which after crystallization from benzene had m.p. 182—184 °C, undepressed on admixture with 2,3-dinitroacetanilide.

2,4-Dinitroaniline (3.0 g) was dissolved in glacial acetic acid (120 ml) and the solution was mixed with conc. hydrochloric acid (24 ml) and kept at 80 °C for 5 hours. After cooling to room temperature the reaction solution was diluted with water (800 ml), extracted with ether, mixed with 50 % hypophosphorous acid (50 ml), kept at room temperature for 5 hours and again extracted with ether. Both ether solutions were washed with aqueous sodium carbonate and water, dried over Na_2SO_4 and decolourized with a little charcoal. The ether was then evaporated.

The first solution gave an oil (1.3 g) which soon solidified. After trituration with light petroleum light-yellow crystals (1.1 g, 33 %), m.p. 49—51 °C, undepressed on admixture with 4-chloro-1,3-dinitrobenzene, were obtained.

The second ether solution yielded a light-yellow liquid (0.9 g, 37 %), $n_D^{20°} = 1.538$. It distilled almost quantitatively in a vacuum (10—12 mm. Hg). The colourless distillate ($n_D^{20°} = 1.546$) crystallized on cooling and melted at *ca.* −25 °C, undepressed on admixture with *m*-dichlorobenzene.

2,5-Dinitroaniline (0.50 g) was dissolved in glacial acetic acid (20 ml), conc. hydrochloric acid (4 ml) was added and the solution was heated to 40 °C for 20 hours. The solution was then worked up as described for 2,3-dinitroaniline. 3,4-Dichloronitrobenzene, obtained in a yield of 0.38 g (72 %), had m.p. 40—42 °C, undepressed on admixture with an authentic sample.

2,6-Dinitroaniline (3.0 g) was dissolved in glacial acetic acid (120 ml), conc. hydrochloric acid (24 ml) was added and the solution heated to 40 °C. After 11 hours (the time varies considerably with the purity of the dinitroaniline) diazonium salts could be detected in the reaction solution. After another 5 hours the solution was worked up as described for 2,4-dinitroaniline.

From the first ether solution, obtained by extraction of the diluted reaction solution, light-yellow crystals (0.53 g, 16 %), m.p. 86—87° C, were obtained. [Calc. for $C_6H_3O_4N_2Cl$

(202.6): C 35.6; H 1.49. Found: C 35.9; H 1.65.] The product was aminated by heating a solution in alcoholic ammonia in a sealed tube to 115—120 °C for 3 hours (*cf.* the amination of 2-chloro-1,3-dinitrobenzene by Borsche and Rantscheff[8]). Pure 2,6-dinitroaniline was obtained, proving the extracted compound to be 2-chloro-1,3-dinitrobenzene.

The second ether solution yielded a light-yellow liquid (1.65 g, 68 %), $n_D^{20°} = 1.542$, which on cooling gave crystals, m.p. *ca.* —26 °C, undepressed on admixture with *m*-dichlorobenzene.

3,4-Dinitroaniline (0.50 g) was heated to 40 °C in a mixture of glacial acetic (20 ml) and conc. hydrochloric acids (4 ml). After 12 hours the reaction solution was worked up as described for 2,3-dinitroaniline. The crude product, m.p. 47—50 °C, obtained in a yield of 0.35 g (67 %), was recrystallized from ethanol to m.p. 54—55 °C, undepressed on admixture with 2,5-dichloronitrobenzene.

The reaction between hydrobromic acid and 2,3-dinitroaniline

2,3-Dinitroaniline (0.50 g) was dissolved in a mixture of glacial acetic (20 ml) and 40 % hydrobromic acids (4 ml). An aqueous solution of sodium nitrite at 60 °C was added to the mixture in portions containing about 0.5 % of the amount theoretically required. After the first addition diazonium salt could be detected in the reaction solution for 20—25 minutes after which time all the diazonium salt had decomposed. After another addition of nitrite more diazonium salt was formed but again decomposed within 20—25 minutes. This procedure was repeated until (after the eleventh addition) no diazonium salt was formed. This means that all the dinitroaniline was diazotised by an amount of nitrite corresponding to *ca.* 5 % of the theoretical. The reaction solution was then diluted with water and neutralized. The precipitate was collected, washed with water and dried. The crude product (0.60 g, 78 %; m.p. 77—79 °C) was crystallized from ethanol yielding light-yellow crystals, m.p. 85—86 °C, undepressed on admixture with 2,3-dibromonitrobenzene.

In another experiment 2,3-dinitroaniline (0.50 g) was heated to 100—110 °C in a sealed tube in a mixture of glacial acetic (20 ml) and 40 % hydrobromic acids (4 ml). After 15 hours the reaction solution was diluted with water, neutralized, and extracted with ether. The ether solution was washed with water, dried and the ether evaporated. The residue (0.45 g) so obtained yielded on steam distillation a light-yellow crystalline product (0.15 g, m.p. 60—65 °C). One crystallization from ligroin gave m.p. 82—83 °C, undepressed on admixture with, 2,3-dibromonitrobenzene. The residue from the distillation was recrystallized three times from benzene giving yellow crystals, m.p. 122—123 °C, undepressed on admixture with 2,3-dinitroaniline.

The reaction between hydrobromic and nitrous acids

Air was aspirated for 40 minutes through a cool (0—5 °C) mixture of glacial acetic (40 ml), propionic (5 ml) and 40 % hydrobromic acids (10 ml) into an acidified silver nitrate solution. A hardly detectable opalescence appeared in the silver nitrate solution. After the addition of sodium nitrite (30 mg), dissolved in a small volume of water, silver bromide precipitated within 5 minutes.

The reaction between hydrochloric acid and 5-chloro-2,4-dinitroaniline

5-Chloro-2,4-dinitroaniline (1.0 g) was suspended in a mixture of glacial acetic (10 ml) and conc. hydrochloric acids (10 ml) and heated. At 70 °C all the chlorodinitroaniline dissolved with formation of diazonium salts and the reaction solution turned reddish-brown. The solution was heated to 95—100 °C and then allowed to cool. After dilution with water (100 ml) it was extracted with ether, mixed with 50 % hypophosphorous acid (20 ml), kept at room temperature for 1 hour and then again extracted with ether. Both ether solutions were washed with aqueous sodium carbonate and water, dried over Na_2SO_4 and decolourized with a little charcoal. The ether was then evaporated.

The first ether solution gave a crystalline product (0.10 g) melting at 75—80 °C. After one crystallization from ligroin pure 1,5-dichloro-2,4-dinitrobenzene (0.07 g, *ca.* 6 %), m.p. 101—102 °C, undepressed on admixture with an authentic sample, was obtained.

The second ether solution yielded a light-yellow oil (0.50 g, 60 %; $n_D^{20°} = 1.568$) which on cooling gave crystals, m.p. 15—16 °C, undepressed on admixture with 1,2,4-trichlorobenzene.

The reaction solution was neutralized and again extracted with ether. No residue was obtained by evaporation of the ether.

SUMMARY

The reaction between hydrochloric acid and the mono- and dinitroanilines has been investigated and discussed. On treatment with hydrochloric acid 2,3-, 2,5-, and 3,4-dinitroaniline are quantitatively converted to chloronitrobenzene diazonium chlorides; 2,4- and 2,6-dinitroaniline yield dichlorobenzene diazonium chloride and chlorodinitrobenzene. The mononitroanilines and 3,5-dinitroaniline remain unchanged.

5-Chloro-2,4-dinitroaniline was found to react in the same way as the above dinitroanilines rather than by the mechanism assumed by Dey, Krishna Maller, and Pai.

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