

Intramolecular Diazotisation of *o*-Nitro-amines

I. The Reaction between 3-Amino-4,9-dinitroretene and Concentrated Hydrochloric Acid

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During an investigation of the salt-forming properties of 3-amino-4,9-dinitroretene, a compound prepared during the synthesis of 4,9-dinitroretene¹, it was found that the substance reacted with conc. hydrochloric acid * in glacial acetic acid solution to give a product that was not the expected amine hydrochloride. When the reaction mixture was refluxed, a gas was evolved and a yellowish-green substance separated. Purification by chromatography and by repeated recrystallisation yielded pale-yellow prisms, melting at 160—161°C **, and analysis showed that two atoms of nitrogen had been eliminated and a chlorine atom had entered the retene molecule. In the present paper, this reaction between conc. hydrochloric acid and 3-amino-4,9-dinitroretene is discussed in detail.

First it was established which of the nitrogen containing groups were eliminated in the reaction. The above mentioned product (m.p. 160—161°C) did not have the properties of an amine, but on reduction it yielded a colourless compound which was proved to be an amine. This indicates that, on treatment with conc. hydrochloric acid, the nitro-amine loses the amino-group and one of the nitro-groups.

The gas evolved in the reaction is odourless, non-inflammable, and does not maintain combustion. It was further investigated in the apparatus, shown on p. 879. In one experiment the gas was conducted directly into the azotometer,

* Conc. hydrochloric acid mentioned in this paper has a density of 1.18.

** All melting points are approximately corrected.

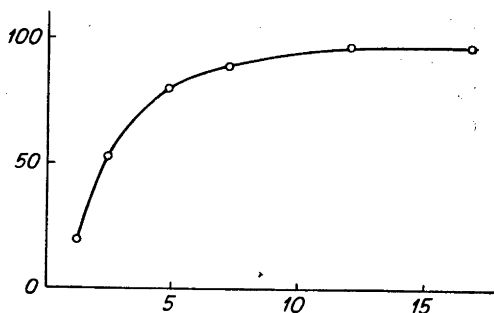


Fig. 1. Relation between yields of the diazonium salt in per cent of the theoretical (ordinate) and amount of conc. hydrochloric acid, expressed as mol HCl/mol of the nitro-amine (abscissa).

in another the gas at first passed through a red-hot tube containing CuO and Cu (charged as for nitrogen analysis according to Dumas). In both cases approximately the same amount of nitrogen/mol of nitro-amine was obtained (see Table 2 on p. 880). Consequently, the gas is probably pure nitrogen, although admixed nitrous oxide cannot be detected in this way.

Thus, on treatment with conc. hydrochloric acid, a glacial acetic acid solution of 3-amino-4,9-dinitroretene gives a product which on warming decomposes with the evolution of nitrogen, and on the basis of this fact, it was assumed that the first-formed product is a diazonium salt. The following experiments supported this assumption. When conc. hydrochloric acid was added to a hot (ca. 100° C) glacial acetic acid solution of the nitro-amine, a faint yellow product (the amine hydrochloride) separated initially, but dissolved in less than half a minute. The yellow solution thus obtained was cooled to room temperature. It reacted with an alkaline solution of β -naphthol forming a red coloured compound, and with cuprous chloride solution or with hypophosphorous acid with evolution of nitrogen. As mentioned above, nitrogen was also evolved if the solution was refluxed.

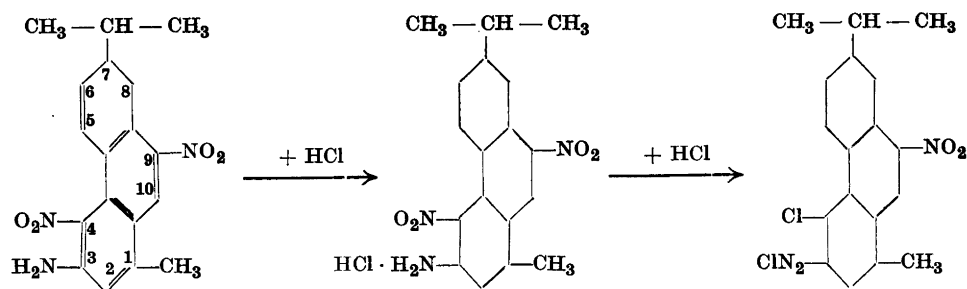
Preliminary experiments showed that the same amount of gas per mol of nitro-amine was evolved when the reaction solution was refluxed for 15—20 minutes or when it reacted with cuprous chloride solution. This tends to indicate that all the gas comes from the diazonium salt and it therefore must consist of pure nitrogen. Consequently, the yield of the diazonium salt can be calculated by measuring the volume of the gas evolved on refluxing the reaction solution. To get an estimate of the relationship between the yield of diazonium salt and the amount of conc. hydrochloric acid used, the following experiments were carried out in the apparatus mentioned above. A known amount of 3-amino-4,9-dinitroretene (ca. 0.170 g) was dissolved in a suitable volume (5 ml) of hot (ca. 100 °C) glacial acetic acid and treated with conc. hydrochloric acid. One or two minutes later, the solution was boiled, and the

nitrogen collected in the azotometer. The results are tabulated on page 880 (Table 3) and in Fig. 1 the yields of diazonium salt are plotted against the amount of added hydrochloric acid. As can be seen from this curve, 7 mols of HCl per mol of nitro-amine gives a yield of about 90 %. It should be emphasized that the time required for the diazotisation reaction to take place at 100 °C seems to be less than one minute, probably as little as 15—30 seconds.

Some experiments were carried out to estimate the speed of the reaction at lower temperatures using an alkaline solution of β -naphthol to detect the presence of the diazonium salt. In a well-stirred suspension of finely powdered nitro-amine hydrochloride (20 mg) in glacial acetic acid (5 ml) and conc. hydrochloric acid (0.5 ml) no diazonium salt was formed during two hours at 25—30 °C, but at a temperature of 35—40 °C, the presence of the diazonium salt could be demonstrated after only 10 minutes.

Some information about the stability of the diazonium salt was obtained by the following experiments. The nitro-amine was dissolved in glacial acetic acid and treated with conc. hydrochloric acid in the usual way. If the solution was refluxed, decomposition was complete in about 10 minutes; at 70 °C about 12 hours were required, while at room temperature, most of the diazonium salt was unchanged even after three days.

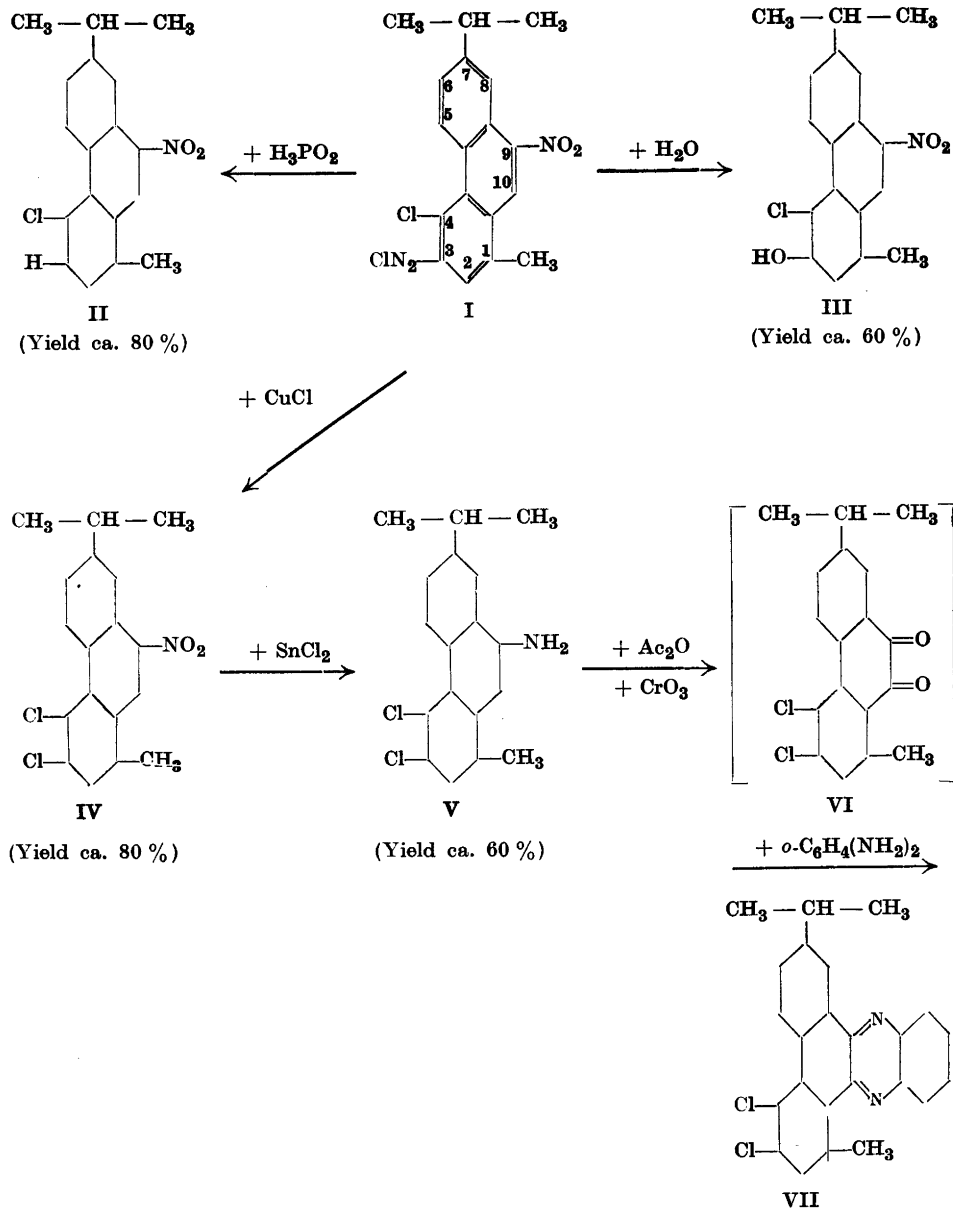
The following reaction scheme seems to be the most probable one for the "intramolecular diazotisation" of 3-amino-4,9-dinitroretene.



On this basis, the yellow product of m. p. 160—161 °C, obtained by refluxing the diazonium salt solution would be expected to be either 3,4-dichloro-9-nitroretene or 3-hydroxy-4-chloro-9-nitroretene. Analyses showed that the former one was obtained, but that 3-hydroxy-4-chloro-9-nitroretene was also present in the crude product.

To establish the empirical formula assumed for the diazonium salt, it was used for the preparation of some simple derivatives of retene (reaction scheme, see p. 875). Analysis figures found for these compounds were in good agree-

ment with the values calculated for the assumed formulae, which therefore must be regarded as correct.



Reaction scheme.

The reaction scheme establishes also, to a certain degree, the structural formulae of the diazonium salt (I) and the derivatives prepared from it. From the synthesis of the quinoxaline (VII) we may conclude that the amine (V) obtained by the reduction of 3,4-dichloro-9-nitroretene (IV) loses the amino-group (acetylated) during its oxidation to the quinone. Therefore, the nitro-group in the 9-position remains unchanged during the intramolecular diazotisation, and it is the nitro-group in the 4-position which is replaced by chlorine. The diazonium salt is formed by reaction between the removed nitro-group and the amino-group in the 3-position.

It remains to be proved if the chlorine atom enters the position vacated by the nitro-group (the 4-position) or if it occupies another position in the retene molecule. Information on this point was not obtained from the reaction scheme above, but proof should be obtainable by conversion of the "4-chloro-9-nitroretene" (II) via the amine to the corresponding chlororetene which could be compared with 4-chlororetene which must be obtainable from 4-nitroretene². These investigations will be discussed in a forthcoming communication, but it seems reasonable to assume that the chlorine atom replaces the nitro-group, and the formulae have been written on this assumption.

It should be pointed out that 3,4-dichloro-9-acetylaminoretene was oxidised to the quinone (VI) under milder conditions than are required for other retene derivatives. This oxidation is usually carried out by the addition of chromic acid to a hot (ca. 100 °C) glacial acetic acid solution of the retene derivative, the quinone as a rule being obtained in yields of 30—50 %. In the case of 3,4-dichloro-9-acetylaminoretene, however, no quinone was formed under these conditions, other oxidation products being obtained. However, if aqueous chromic acid was used and the temperature kept at 40 °C, the quinone (VI) was obtained in a probable yield of about 10 %. Because of the low yield and the formation of a large quantity of other oxidation products, the quinone was not isolated in a pure state, but the crude product was allowed to react with *o*-phenylene diamine. The sparingly soluble quinoxaline (VII) which formed, could then be readily isolated.

When the diazonium salt was heated with water, 3-hydroxy-4-chloro-9-nitroretene (III) was obtained although in rather low yield. However, the compound was easily isolated in a pure state by chromatographic purification. The crude product was dissolved in benzene and adsorbed on a column of alumina. Development with benzene gave a distinct red band which moved very slowly and which contained fairly pure 3-hydroxy-4-chloro-9-nitroretene. Washing with acetone removed some impurities but the main band was not eluted although its colour changed from red to paleyellow, a colour change

which could be reversed by the addition of benzene. Acetone, containing a few per cent of conc. hydrochloric acid, proved to be a very good eluant.

It may be mentioned that 3-hydroxy-4-chloro-9-nitroretene can be used as an acid-base indicator. An acidic solution of the compound in dilute ethanol has a pale yellow colour at high concentrations, but is nearly colourless in concentrations suitable for indicators; on the addition of alkali the ethanolic solution turns a blood-red colour which on dilution changes to orange or orange-red. The compound is very sparingly soluble in water, but a very dilute aqueous solution may be obtained by adding an ethanolic solution to water. By using buffers of different pH, the interval for the colour change was determined to be pH 8.5—9.5.

The intramolecular diazotisation described in this paper, takes place with other *o*-nitro-amines. Under the same conditions as those used for 3-amino-4,9-dinitroretene, diazonium salts were formed, apparently in good yields, from 3-amino-4-nitroretene and 1-nitro-2-naphthylamine. With *o*-nitro-amines of the benzene series some experiments were carried out, but no diazonium salt has been obtained as yet. The general applicability of the intramolecular diazotisation will be further investigated.

Investigations of the conditions for intramolecular diazotisation have shown that the hydrochloric acid may be replaced by hydrobromic acid (d, 1.38), without changing the reaction conditions. The diazonium bromide has not been closely investigated, although its presence was indicated by the reactions with alkaline β -naphthol solution (intense red colour) and with cuprous chloride solution (evolution of nitrogen). The addition of hydriodic acid (d, 1.70) to a hot glacial acetic acid solution of 3-amino-4,9-dinitroretene caused an immediate evolution of gas, possibly due to the decomposition of a diazonium iodide initially formed. Owing to the instability of diazonium iodides, these cannot be detected by means of β -naphthol or cuprous chloride. Consequently, the evolved gas was investigated in the apparatus described on page 879, and shown to be nitric oxide in amount corresponding to ca. 1 mol per mol of the nitro-amine. Though the remaining reaction product has not been investigated, it seems safe to assume that no diazonium iodide is formed by treating the nitro-amine with hydriodic acid. The nitro-group in the 4-position is apparently reduced by the hydriodic acid either before or after the exchange reaction. These reactions between *o*-nitro-amines and hydrobromic and hydriodic acids will be further investigated.

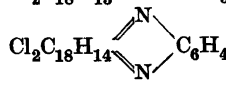
During the investigation of the intramolecular diazotisation attempts were made to use solvents other than glacial acetic acid and it was found that other carboxylic acids (formic, propionic, *n*-valeric, and lactic acids) were useful solvents. With solvents such as ethanol or acetone no diazonium salts were

obtained, the nitro-amine being recovered unchanged and it seems possible that carboxylic acids are the only solvents which can be employed.

The intramolecular diazotisation of *o*-nitro-amines, described in this paper, does not appear to have been reported in the literature. However, it is known that a nitro-group, attached directly to a carbon atom in an aromatic ring can be activated by suitable substitution of groups in the molecule (see, *e. g.*, Degering in *An outline of organic nitrogen compounds*³) and the nitro-group is often especially mobile in compounds containing a diazonium-group. Thus it has been observed that many nitro-amines must be diazotised in non-aqueous solution; otherwise the nitro-group is replaced by a hydroxyl-group and a diazo-oxide may be formed⁴. Further, the influence of a diazonium-group is observed in a reaction similar to the intramolecular diazotisation. It has been found that, on diazotisation in a solution containing chloride ions, some aromatic nitro-amines exchange the nitro-group for chlorine. *E. g.*, 1-nitro-2-naphthylamine⁵⁻⁸, 2,3-dinitro-4-methoxyaniline⁹, 2,5-dichloro-4-nitro-aniline¹⁰, 4-chloro-5-nitro-2-aminoacetophenone¹¹, 4-chloro-3-nitro-2-aminoacetophenone¹¹, and 4-chloro-2-nitro-3-aminoacetophenone¹². It may be of interest to establish if intramolecular diazotisation can be carried out with these compounds as well. To date, only 1-nitro-2-naphthylamine has been tested and, as mentioned above, intramolecular diazotisation does indeed take place, the diazonium salt apparently being obtained in very good yield.

Atkinson and Simpson¹¹ have investigated the diazotisation of 4-chloro-5-nitro-2-aminoacetophenone in the presence of chloride ions. Their observations showed "that a substituted diazonium kation may become involved in an exchange of groups before removal of the diazonium residue, and that slight

Table 1. New compounds prepared in the present investigation.

Name	Formula	M. p. °C
4-Chloro-9-nitroretene-3-diazonium chloride	$\text{Cl}(\text{NO}_2)\text{C}_{18}\text{H}_{15}\text{N}_2\text{Cl}$	—
3,4-Dichloro-9-nitroretene	$\text{Cl}_2\text{C}_{18}\text{H}_{15}\text{NO}_2$	160—161
3,4-Dichloro-9-aminoretene	$\text{Cl}_2\text{C}_{18}\text{H}_{15}\text{NH}_2$	122—123
3,4-Dichloro-9-acetylaminoretene	$\text{Cl}_2\text{C}_{18}\text{H}_{15}\text{NHCOCH}_3$	248—249
3,4-Dichlororetenequinoxaline *		133—134
4-Chloro-9-nitroretene	$\text{ClC}_{18}\text{H}_{16}\text{NO}_2$	133—134
3-Hydroxy-4-chloro-9-nitroretene	$\text{HO}(\text{Cl})\text{C}_{18}\text{H}_{15}\text{NO}_2$	170—171
3-Acetoxy-4-chloro-9-nitroretene	$\text{CH}_3\text{COO}(\text{Cl})\text{C}_{18}\text{H}_{15}\text{NO}_2$	137—138

* See note on page 882.

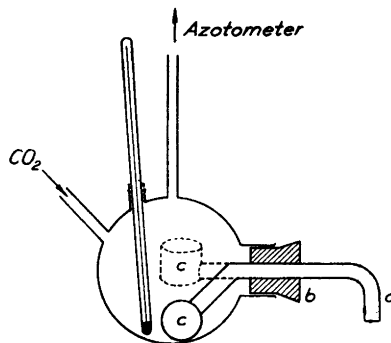


Fig. 2. Apparatus, used for quantitative investigations of the intramolecular diazotisation.

variations in the experimental conditions, such as gentle warming, may suffice to determine whether or not such an interchange occurs". Intramolecular diazotisation cannot proceed by this mechanism as the diazonium cation cannot be formed before the nitro-group is split off. Perhaps the essential step is the reaction of the hydrochloric acid with a compound formed from the nitro-amine and the carboxylic acid used as the reaction medium. As yet we know, however, too little about this transformation to be able to say anything about its mechanism. The investigation of the intramolecular diazotisation reaction will be continued.

EXPERIMENTAL

I. Investigation of the reaction between 3-amino-4,9-dinitroretene and concentrated hydrochloric acid

A. Analysis of the evolved gas

The apparatus used for this investigation is schematically drawn in Fig. 2. In the 50-ml round-bottomed flask, 3-amino-4,9-dinitroretene (ca. 5×10^{-4} mol) was suspended in glacial acetic acid (5 ml). On the glassrod (a), through the rubber stopper (b) was fixed a small container (c) containing a mixture of conc. hydrochloric acid and glacial acetic acid (1.5 ml) corresponding to 0.70 ml of conc. hydrochloric acid. A glass tube connected the flask to an azotometer, containing 50 % aqueous potassium hydroxide. Carbon dioxide was passed through the apparatus until micro bubbles were obtained in the azotometer and the suspension in the flask was heated to about 100°C to obtain a clear solution. By turning the glassrod (a) the acid mixture in the container (c) was added, and, after 1–2 minutes, the reaction mixture was boiled for 15 minutes. While boiling was continued, carbon dioxide was again passed through the apparatus until micro bubbles appeared in the azotometer. The volume, temperature, and pressure of the collected gas was determined. The experiment was repeated, using a modified apparatus in which the gas, before entering the azotometer, was passed through a red-hot tube, charged with CuO and Cu as for nitrogen analysis according to Dumas. The results of these experiments are listed in Table 2 and it can be seen that approximately the same volume of gas was obtained in both cases. This indicates that the gas, which was odourless, non-inflammable, and not able to maintain combustion, consisted of pure nitrogen.

Table 2. The results of the investigation of the evolved gas.

3-Amino-4,9-dinitroretene mol $\times 10^4$	Gas, collected in the azotometer					Remarks
	Temp. °C	Pressure mm Hg	Volume ml	Volume at N.T.P. ml	Vol./mol of nitro- amine l	
5.010	21	758	11.88	11.00	22.0	
5.013	22	766	11.75	10.96	21.9	
5.019	18	766	11.48	10.86	21.6	Cu-CuO-tube
5.010	19	746	11.92	10.94	21.8	Cu-CuO-tube

B. The relationship between the amount of concentrated hydrochloric acid and the yield of diazonium salt

In the same way as before a series of intra molecular diazotisations were carried out, using varying amounts of conc. hydrochloric acid. The evolved gas did not pass through the combustion tube in these experiments. The hydrochloric acid was added mixed with 2–5 vol. of glacial acetic acid and the total volume of glacial acetic acid in the reaction mixture was, in each case 5 ml. From the amount of nitrogen collected in the azotometer, the yield of diazonium salt was calculated. The results are listed in Table 3 and in the curve in Fig. 1 (p. 873) the yields of diazonium salt are plotted against the amount of conc. hydrochloric acid added.

Table 3. Yields of the diazonium salt with varying amounts of concentrated hydrochloric acid.

3-Amino-4,9-dinitroretene mol $\times 10^4$	Hydrogen chloride		Nitrogen			Diazonium salt yield of the theoretical	
	12 M HCl	mol HCl per mol of nitro- amine	Temp.	Pressure	Volume	%	% aver.
	ml		°C	mm Hg	ml		
5.016	0.05	1.2	23	742	2.44	19.6	
5.001	0.05	1.2	23	760	2.34	19.3	19.5
5.004	0.10	2.4	25	742	6.80	54.3	
5.010	0.10	2.4	24	742	6.40	51.2	52.7
4.995	0.20	4.8	23	762	9.77	80.8	
5.007	0.20	4.8	24	742	9.92	79.4	80.1
5.004	0.30	7.2	21	750	10.68	87.3	
5.007	0.30	7.2	23	762	10.92	90.0	88.7
4.992	0.50	12.0	22	755	11.67	96.0	
5.022	0.50	12.0	22	765	11.82	97.9	96.9
5.019	0.70	16.7	18	766	11.48	96.6	
5.013	0.70	16.8	22	766	11.75	97.6	97.1

C. Suitable conditions for the intramolecular diazotisation of 3-amino-4,9-dinitroretene

Conc. hydrochloric acid (5 ml) was added to a stirred solution of 3-amino-4,9-dinitroretene (2.0 g) in hot (ca. 100° C) glacial acetic acid (60 ml). The amine hydrochloride first formed, dissolved immediately yielding 4-chloro-9-nitroretene-3-diazonium chloride and after 1–2 minutes the solution was cooled to room temperature. Diazonium salt solutions, prepared in this way, were used for the syntheses described below.

II. Derivatives prepared from 4-chloro-9-nitroretene-3-diazonium chloride

3, 4-Dichloro-9-nitroretene

3-Amino-4,9-dinitroretene (2.0 g) was diazotised as described above and the diazonium salt solution was added to a boiling solution containing cuprous chloride (10 g) in conc. hydrochloric acid (100 ml). A yellowish-green product separated (2.0 g), which after one crystallisation from glacial acetic acid (12 ml) was dissolved in a mixture of 15 ml of benzene and 10 ml of petroleum ether (b. p. 40–50 °C) and adsorbed on a column of alumina (18 × 3.5 cm). Elution with petroleum ether, containing about 10 % of benzene, yielded a pale-yellow residue (1.70 g) which melted at 157–158 °C, and after one crystallisation from glacial acetic acid gave pure 3,4-dichloro-9-nitroretene (1.50 g) as pale-yellow prisms melting at 160–161 °C. The yield corresponds to 73 % of the theoretical, calculated on the amount of 3-amino-4,9-dinitroretene consumed. The compound is easily soluble in chloroform and benzene, rather soluble in ethanol, glacial acetic acid, and acetone, and slightly soluble in ligroin.

$C_{18}H_{15}Cl_2NO_2$ (348.2)	Calc.	C 62.1	H 4.34	N 4.02	Cl 20.4
	Found	» 62.2	» 4.36	» 4.00	» 20.3

3, 4-Dichloro-9-aminoretene

Finely powdered 3,4-dichloro-9-nitroretene (2.9 g) was suspended in a solution of $SnCl_2 \cdot 2H_2O$ (12 g) in glacial acetic acid (60 ml) saturated with hydrogen chloride and stirred at 20° C for two hours. The nitro-compound dissolved gradually and the white crystalline reaction product which separated was filtered off after some hours and washed with dilute hydrochloric acid and ether then suspended in ether and washed with aqueous alkali. Evaporation of the ether yielded 3,4-dichloro-9-aminoretene (1.6 g) of m. p. 117–119 °C – 60 % of the theoretical. After one crystallisation from ethanol or from ligroin-benzene, the amine was obtained as colourless plates melting at 122–123 °C.

$C_{18}H_{17}Cl_2N$ (318.2)	Calc.	C 67.9	H 5.39
	Found	» 67.6	» 5.44

3,4-Dichloro-9-aminoretene was easily diazotised, and the diazonium salt gave a red azo-compound with β -naphthol.

The *hydrochloride* crystallised as white needles (m. p. 226–228 °C, decomp.) when conc. hydrochloric acid was added to a hot ethanolic solution of the amine and the solution allowed to cool.

$C_{18}H_{18}Cl_3N$ (354.7)	Calc.	C	60.9	H	5.11
	Found	»	61.0	»	5.15

Picrate. 3,4-Dichloro-9-aminoretene (0.1 g) and picric acid (0.15 g) were dissolved in ca. 5 ml of hot ethanol. On cooling, the picrate separated as short, yellow needles melting at ca. 176–178 °C (decomp.).

$C_{24}H_{20}Cl_2N_4O_7$ (547.3)	Calc.	C	52.7	H	3.68
	Found	»	52.8	»	3.75

3,4-Dichloro-9-acetylaminoretene. Acetic anhydride (2 ml) was at room temperature added to a solution of 3,4-dichloro-9-aminoretene (2.0 g) in benzene (15 ml). Within one minute, the acetyl derivative separated as thin, white, needle-shaped crystals (2.0 g, 90 %) which were collected after one hour. The compound thus prepared was pure and melted at 248–249 °C.

$C_{20}H_{19}Cl_2NO$ (360.3)	Calc.	C	66.7	H	5.32
	Found	»	66.7	»	5.25

3,4-Dichlororetenequinoxaline *

A solution of CrO_3 (0.8 g) in water (3 ml) was added with stirring to a suspension of 3,4-dichloro-9-acetylaminoretene in glacial acetic acid (10 ml) at 40 °C. After 10 minutes the dark solution was diluted with water and the precipitated product collected, washed with water, and dissolved in hot ethanol containing *o*-phenylene diamine (ca. 0.1 g). On cooling, 3,4-dichlororetenequinoxaline (0.03 g) crystallised as pale-yellow needles, m. p. 132–133 °C. The yield was only ca. 7 %, calculated on the 3,4-dichloro-9-acetylaminoretene consumed. The quinoxaline was crystallised from *n*-propanol and then melted at 133–134 °C.

$C_{24}H_{18}Cl_2N_2$ (405.3)	Calc.	C	71.1	H	4.48	Cl	17.5	N	6.91
	Found	»	71.1	»	4.60	»	17.3	»	6.97

The quinoxaline dissolves in conc. sulphuric acid giving an intense red colour which disappears on dilution with water.

4-Chloro-9-nitroretene

3-Amino-4,9-dinitroretene (2.0 g) was diazotised as described above (C) and 20 ml of hypophosphorous acid (50 %) was added at room temperature. Nitrogen was evolved and a yellow product separated within a few minutes. When the reduction had proceeded

* About the name of this type of compound, see *Acta Chem. Scand.* 2 (1948) 487.

for one hour, the product (1.7 g, m. p. 125–127 °C) was filtered off, washed with dilute acetic acid, dissolved in a mixture of benzene (10 ml) and petroleum ether (10 ml, b. p. 40–50 °C) and adsorbed on a column of alumina (15 × 3.5 cm). Development with a mixture of 5 vol. of petroleum ether and 1 vol. of benzene gave a yellow band, which was eluted with the same solvent. The eluate was decolourised with charcoal and yielded 1.45 g of product of m. p. 130–131 °C. (Yield: 78 %, calculated on 3-amino-4,9-dinitroretene consumed). One crystallisation from *n*-propanol or glacial acetic acid gave pure 4-chloro-9-nitroretene as flat prisms, melting at 133–134 °C, easily soluble in benzene, acetone, and chloroform, and slightly soluble in ligroin and ethanol.

$C_{18}H_{16}ClNO_2$ (313.8)	Calc.	C 68.9	H 5.14	Cl 11.30	N 4.46
	Found	» 68.8	» 5.16	» 11.1	» 4.44

3-Hydroxy-4-chloro-9-nitroretene

3-Amino-4,9-dinitroretene (1.0 g) was diazotised as above (C). Water (5 ml) was added to the diazonium salt solution which was then heated on a boiling water-bath for four hours. More water was then added to the reaction mixture to ensure complete precipitation of the 3-hydroxy-4-chloro-9-nitroretene formed in the reaction. The crude product was dissolved in benzene and adsorbed on a column of alumina (15 × 3.5 cm). Development with benzene gave a sharp red band. Washing with acetone removed some impurities, but the main band was not eluted, although it turned pale yellow in colour. The band was eluted with acetone containing a few per cent of conc. hydrochloric acid, the eluant diluted with water and extracted with ether. Evaporation of the washed ether solution gave a crystalline residue (0.30 g) of almost pure 3-hydroxy-4-chloro-9-nitroretene (m. p. 166–167 °C; yield 32 %). The product was further purified by crystallisation from ligroin-benzene and then formed yellow prisms melting at 170–171 °C, easily soluble in most organic solvents

$C_{18}H_{16}ClNO_3$ (329.8)	Calc.	C 65.6	H 4.89	Cl 10.7	N 4.25
	Found	» 65.5	» 5.01	» 10.6	» 4.32

An alcoholic solution of 3-hydroxy-4-chloro-9-nitroretene turns blood-red on the addition of aqueous alkali. Despite its low solubility in water, the compound can be used as an acid-base indicator. By adding the alcoholic solution to buffers (sodium hydroxide-boric acid) of different pH the interval for the colour change was determined to be pH 8.5–9.5.

3-Acetoxy-4-chloro-9-nitroretene was prepared by refluxing a solution of 3-hydroxy-4-chloro-9-nitroretene (0.1 g), acetic anhydride (2 ml), and sodium acetate (0.1 g) for one hour. On cooling, the acetyl derivative separated as nearly colourless, very thin, short, needles melting at 136–137 °C. Crystallisation from glacial acetic acid yielded the pure compound, m. p. 137–138 °C.

$C_{20}H_{18}ClNO_4$ (371.8)	Calc.	C 64.6	H 4.88
	Found	» 64.6	» 4.92

SUMMARY

A new reaction for *o*-nitro-amines has been investigated and discussed. This reaction, termed in the present paper intramolecular diazotisation, consists the conversion of an *o*-nitro-amine to a chlorine substituted diazonium chloride by treatment with concentrated hydrochloric acid alone. For a closer study of the reaction, 3-amino-4,9-dinitroretene was used, and the product, 4-chloro-9-nitroretene-3-diazonium chloride, was characterised by the formation of several derivatives. The reaction was demonstrated to be applicable to 1-nitro-2-naphthylamine and 3-amino-4-nitroretene. *o*-Nitro-amines of the benzene series do not appear to undergo this reaction.

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