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Investigations in the Retene Field

I. Determination of the Structure of 4-Nitro-3-acetaminoretene

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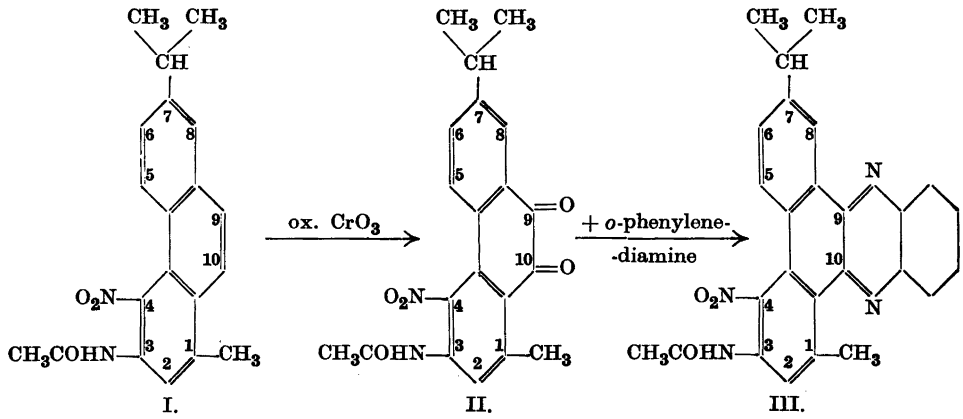
In many earlier works on retene attempts have been described to obtain pure nitroretenes by means of direct nitration [1—3]. These experiments have not given satisfactory results, since only viscous impure products were obtained. Recently, however, some Danish workers have succeeded in performing more successful nitration. They thus obtained, on cautious nitration of retene, 9-nitroretene in a yield of approximately 5 per cent of the theoretical [2]. Since, however, the method requires chromatography and molecular distillation in order to obtain a pure product, it is not as yet particularly suitable for use in the production of nitroretene.

In order if possible to throw some light on the problem of the nitration of retene, it is my intention in this and subsequent investigations to prepare a series of nitroretenes and determine their structure. It may be of some value to obtain a more thorough knowledge of those products that can be formed by nitration of retene. In the methods of preparation described in the following, 3-acetaminoretene was used as the starting material, since this compound is easily nitrated and the amino group can be eliminated by diazotization [3]. The nitration of 3-acetaminoretene is described in earlier papers [3]. Under mild conditions of nitration, two mononitro derivatives are obtained simultaneously, *i. e.* 9-nitro-3-acetaminoretene and x-nitro-3-acetaminoretene. The derivatives were obtained in the approximate proportion of 3 : 2, the 9-derivative giving the largest yield. It is demonstrated in the present investigation that x-nitro-3-acetaminoretene, whose structure was hitherto unknown, has the nitro group in the 4-position. It can be mentioned in this connexion that among the previously produced derivatives of retene of known structure there is none that has any substituent on carbon 4.

In setting up the formulae for the structures it was assumed that the position of the nitro group in x-nitro-3-acetaminoretene was known. It was thus simpler to draw the formulae and the reaction series were more easy to survey. In order to obtain a simpler name, the designation »retenequinoxaline» is used instead, for example, of 3″-methyl-5′-iso-propyl-(dibenso-1′,2′: 1,2 ; 1″,2″ : 3,4-phenazine). The original position numbering of the retene molecule has been retained for derivatives of retenequinoxaline, thus indicating more satisfactorily their relations with the retenequinone derivatives from which they were produced.

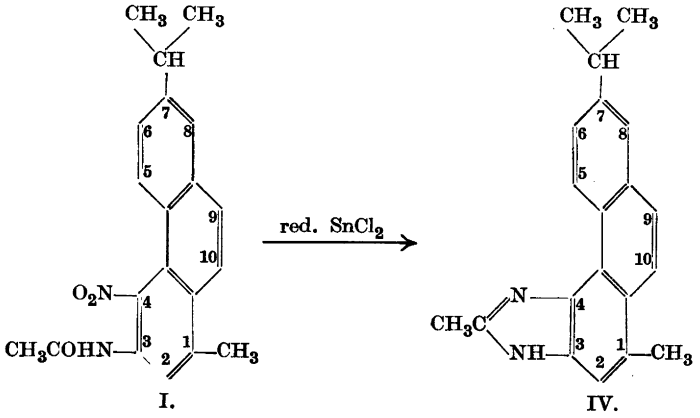
As pointed out in the foregoing, two mononitro derivatives, of which one has the nitro group in the 9-position, are obtained on mild nitration of 3-acetaminoretene. In a preliminary investigation it was established that the nitro group of x-nitro-3-acetaminoretene (I) was not in the 10-position. This was done by transferring the compound to quinone (II) by means of oxidation with chromic trioxide. Since the quinone also contained two nitrogen atoms, it could immediately be established that the nitro group must be bound to a carbon atom in one of the other two benzene nuclei. Had this not been the case, the nitro group would have been eliminated on oxidation. In order to check that quinone had been formed, x-nitro-3-acetaminoretenequinoxaline (III) was also prepared.



I. II. III.

From previous experiments[3] it was known that the acetyl group in 9-nitro-3-acetaminoretene is easily split off by boiling the compound in glacial acetic acid containing concentrated hydrochloric acid. We were not successful in producing x-nitro-3-retylamine hydrochloride in a similar manner. In attempts to split off the acetyl group in an alkaline solution, an intensely dark-red oil was formed which did not invite further treatment. This was, however, later identified as somewhat impure x-nitro-3-aminoretene.

In the hope of obtaining a compound more easy to work with, x-nitro-3-acetaminoretene was reduced with stannous chloride in a solution of glacial acetic acid containing a considerable quantity of concentrated hydrochloric acid. A white product was obtained that formed salts with acids and that could be readily acetylated with acetic anhydride. The values obtained on analysis and the fact that it was not possible to diazotize the compound indicated that something other than an amine was present. The analytical values are in good agreement with the theoretical values if we assume that an imidazole ring was formed (IV). This ring formation shows that the nitro group must be ortho to the acetylated amino group in the 3-position, thus either in the 2- or 4-position.



I. IV.

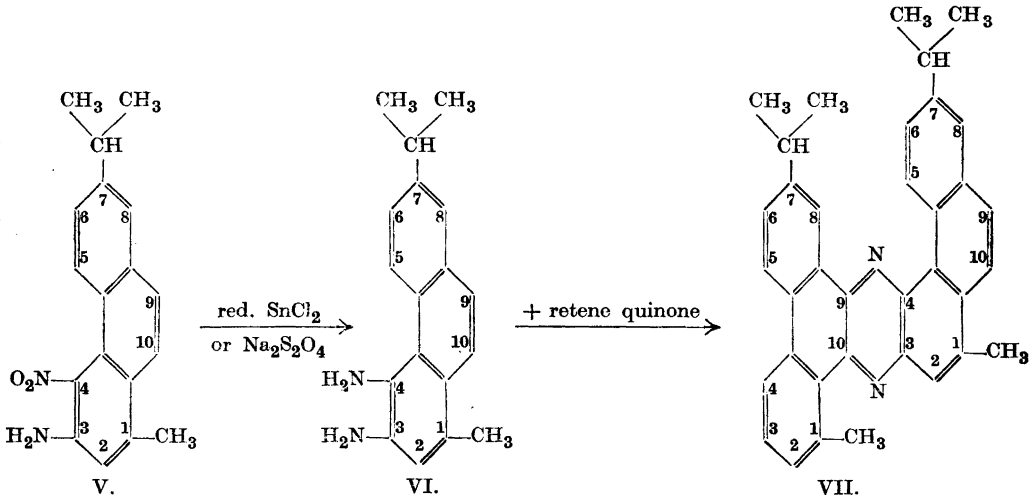
Analysis value:	Found	C 83.4	H 7.07	N 9.64
For the imidazole	Calc.	» 83.3	» 6.99	» 9.72
For x-amino-3-acetamino-retene	Calc.	» 78.4	» 7.24	» 9.15

In order to define (IV) more accurately, some simple derivatives were produced from it, such as the hydrochloride, the N-acetyl derivative and the picrate. Like other imidazoles of the same type, (IV) forms a very poorly soluble picrate.

Attempts were also made to reduce x-nitro-3-acetaminoretene in ethanol solution with sodium sulphide. This resulted in a product similar to that obtained in attempts to split off the acetyl group in alkaline solution (see foregoing). The dark-red oil was extracted in ether. On the introduction of hydrogen chloride into the dry ether solution, the hydrochloride of x-nitro-3-aminoretene was obtained, the yield being approximately 90 per cent of the theoretical. The nitroamine (V) could be diazotized, and yielded on acetyla-

tion the initial product (I). The sodium sulphide had thus not reduced the nitro group but had only acted as an alkali and had caused a splitting off of the acetyl group. As is clear from the description of the synthesis in the following, potassium hydroxide was subsequently used as an alkaliser instead of sodium sulphide. Under suitable conditions, the nitroamine was not obtained as an oily product but directly in crystallized form, analytically pure and with a yield of approximately 80 per cent of the theoretical.

The production of (IV) shows, as already pointed out, that the nitro group must be substituted in the ortho position to the amino group. In order to establish this more definitely, 3,x-diaminoretene (VI) was produced, which should give the reactions of an ortho-diamine. This was found to be the case. The diamine thus reacted with retenequinone by forming a quinoxaline (VII).



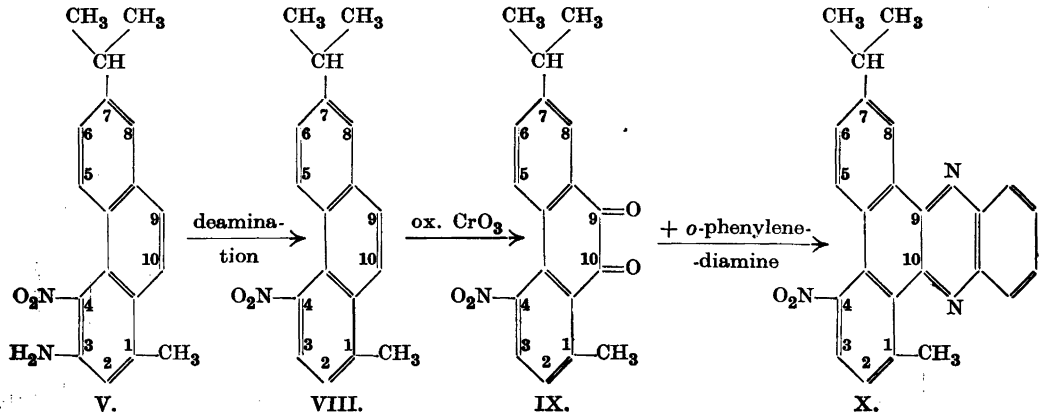
V. VI. VII.

As seen from the foregoing, the nitro group must occupy the 2- or 4-position. Two methods are available for determining which of these two possibilities was present. In both cases the nitroamine is deaminated and x-nitroretene (VIII) thus obtained. This compound can in turn either be transferred via x-aminoretene to x-hydroxyretene — which is compared with the known 2-hydroxyretene [4] — or can be oxidized to x-nitroretenequinone which is compared with 2-nitroretenequinone [5] recently obtained.

The first reaction series, which is not included in the description of the syntheses, was performed qualitatively by diazotization of the x-aminoretene and heating of the diazonium salt. A crystallized substance, too impure for analysis, was obtained, which was probably the x-hydroxyretene. This couples

with diazonium salts with formation of intensive colour. Since the 2-hydroxyretene does not couple, the hydroxyretene formed must therefore be a 4-derivative.

The other reaction series was performed under more accurate conditions. On oxidation of the x-nitroretene (VIII) with chromium trioxide a quinone (IX) was obtained which had its melting point at 185.0—185.5 °C. It crystallized as long yellow needles and reacted with o-phenylenediamine with the formation of a quinoxaline (X). 2-Nitroretenequinone melts at approximately 220 °C and crystallizes as flakes. Thus it can not be identical with x-nitroretenequinone which must, consequently, have the nitro group in the 4-position.



V. VIII. IX. X.

Since the structure of 4-nitro-3-acetaminoretene is known through the foregoing experiments, another structural problem is also solved at the same time. In an earlier investigation it was namely demonstrated that on stronger nitration of 9-nitro-3-acetaminoretene, a dinitro derivative is obtained that is identical with the dinitro-3-acetaminoretene formed when 4-nitro-3-acetaminoretene is exposed to further nitration. This dinitro derivative has thus one nitro group in common with 9-nitro-3-acetaminoretene and one with 4-nitro-3-acetaminoretene. Its formula must therefore be 4,9-dinitro-3-acetaminoretene.

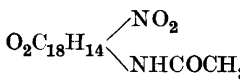
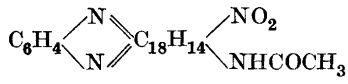
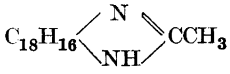
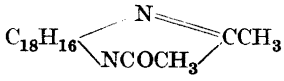
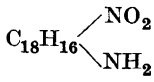
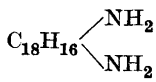
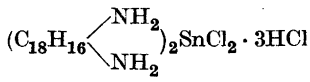
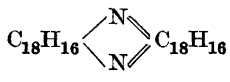
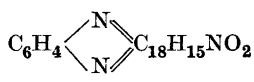
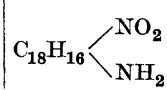
In addition to those substances that are essential to demonstrate the structure, others have been included in this investigation that are in close connexion with the proof of the structure as well as those which contribute towards characterizing the new compounds. Thus the hydrochloride and the picrate have been produced from the diaminoretene. A stannous complex with 3,4-diaminoretene was also isolated. On reduction of 4-nitro-3-aminoretene with stannous chloride in an ethanol solution containing hydrochloric

acid, the first product obtained was not the hydrochloride of the diamine but the complex of the hydrochloride with tin. This crystallized as long flat needles. Since a closer analysis of this complex is not within the scope of this investigation, I confined myself to analyzing all the elements comprising the complex and to calculating the empirical formula with the guidance of the analytic figures. The formula was found to be $\left(C_{18}H_{16}\begin{matrix}NH_2\\NH_2\end{matrix}\right)_2SnCl_2 \cdot 3HCl$. A reservation must be made for the number of hydrogen atoms, since a change of one or two such atoms has only a very slight effect on the percentage of hydrogen. The complex can also be produced directly from diamine and stannous chloride. Attempts to obtain it from stannic ion solution did not succeed. The tin atom in the complex must consequently be considered to be bivalent.

In the course of this investigation additional substances were also obtained, but it was not possible to determine the exact conditions of their synthesis and formulae. Thus 4-nitro- and 9-nitro-3-aminoretene at times crystallized in a dark red form instead of the reddish-yellow one usually obtained. It is probable, at any rate in the case of the 4-derivative, that the dark red form is a molecular combination with the solvent (ethanol or methanol). On reduction of 4-nitro-3-aminoretene, a product with m. p. 95 °C was isolated simultaneously with the 3,4-diaminoretene with m. p. 81 °C, the synthesis of which is described in the following. The former compound reacts with retenequinone to give a quinoxaline which has the same m. p. as the quinoxaline produced from the 81-degree diamine. No depression in the m. p. (300 °C) was achieved on mixing the two quinoxalines. Since the form with m. p. 95 °C also appears to be a diamine, and since the quinoxalines are presumably identical, it appears probable that it is only another form of 3,4-diaminoretene.

Finally, the previous assumption that 9-nitro-3-aminoretene is unstable in air [3] must be revised. The assumption is based on the following observation. If the hydrochloride of the nitroamine is suspended in ether and shaken with a solution of sodium carbonate, a yellow solution is obtained. If this is dropped on a filter paper, a yellow blot is formed which becomes intensely red when the ether has evaporated. The red colour was assumed to depend on the effect of the air. Closer investigation showed that the nitroamine, which is itself reddish-yellow, gives a pale yellow solution in ether. When the ether evaporates, the red-coloured nitroamine is once more obtained. The red colour is thus not caused by the nitroamine being discoloured in some way when it is exposed to air. That the red substance really is 9-nitro-3-aminoretene is demonstrated by the fact that on acetylation it yields 9-nitro-3-acetaminoretene. Moreover, the analytical values of both the nitroamine and its picrate show that this assumption is correct.

Table 1. Substances produced in the present investigation. (Picrates and hydrochlorides not included.)

No.	Name	Formula	M. p. °C *
2.	4-Nitro-3-acetaminoretene-quinone		187—188
3.	4-Nitro-3-acetaminoretene-quinoxaline		305 (decomp.)
4.	2-Methylretimidazole-(3′,4′)		199.0—199.5
5.	N-Acetyl-2-methylretimid-azole-(3′,4′)		202—203
6.	4-Nitro-3-aminoretene		124—125
7.	3,4-Diaminoretene		80—81
8.	3,4-Diaminoretene's tin complex		approx. 190
9.	Reto-3′,4′ : 2,3-reto-9″,10″ : 5,6-pyrazine		299—300
10.	4-Nitroretene	$C_{18}H_{17}NO_2$	136—137
11.	4-Nitroretenequinone	$O_2C_{18}H_{15}NO_2$	185.0—185.5
12.	4-Nitroretenequinoxaline		175—176
13.	9-Nitro-3-aminoretene		152—153

* The melting points are approximately corrected.

A modified method for the production of 4-nitro-3-acetaminoretene is described in the experimental part of this paper. The essential difference lies in the manner of separating 9-nitro-3-acetaminoretene from 4-nitro-3-acetaminoretene. The method is based on the fact that the 9-derivative is practically insoluble in benzene, whereas the 4-derivative is fairly soluble. The isomer mixture is therefore extracted with benzene and the derivative soluble in it is recrystallized in glacial acetic acid. In this way very pure 4-nitro-3-acetaminoretene is obtained. The compound insoluble in benzene consisted of practically pure 9-nitro-3-acetaminoretene.

EXPERIMENTAL PART

1. 4-Nitro-3-acetaminoretene

30 g of 3-acetaminoretene suspended in 225 ml of glacial acetic acid was mixed with 70 ml of propionic acid. (The propionic acid was added in order to prevent the glacial acetic acid from crystallizing when it was cooled to approximately 10° C). 180 ml of a mixture of concentrated nitric acid (d = 1.4) and 70 ml of glacial acetic acid was added in drops with vigorous stirring during approximately 20 minutes. The temperature was kept at 5—10° C. During nitration the reaction mixture was at first a thin fluid, then thickened considerably and once more became more thinly fluid. After the nitric acid had been added, nitration was allowed to continue for 35 minutes. The yellow reaction product was filtered off, thoroughly washed with water and dried. This crude product (30 g) was boiled with 250 ml of benzene and the mixture allowed to cool to 30—40 °C. The residue was filtered off and once more extracted with 150 ml of benzene. In the benzene solution practically only 4-nitro-3-acetaminoretene was present. The benzene was distilled off and the residue crystallized in 130 ml of glacial acetic acid. The crystals containing acetic acid thus obtained were dried at 125° C and the acetic acid thereby eliminated. The yield of the pure product was 12.5 g, m. p. 196—197° C.

The substance insoluble in benzene consisted of practically pure 9-nitro-3-acetaminoretene, m. p. 284—285 ° C. A recrystallization in glacial acetic acid gave an analytically pure product.

2. 4-Nitro-3-acetaminoretenequinone

10 g of chromium trioxide was added in portions to a suspension of 5.0 g of 4-nitro-3-acetaminoretene in 25 ml of glacial acetic acid. The heat of the reaction caused the temperature to rise to 100—110° C. Oxidation proceeded for 25 minutes. 200 ml of water was then added in drops. A yellow precipitate of the quinone then appeared. This was filtered off and washed carefully with water. The yield was 2.3 g. After recrystallization in glacial acetic acid (1.5 g in 5 ml) a pure 4-nitro-3-acetaminoretenequinone, m. p. 187—188° C, was obtained. It crystallized as flat yellow prisms.

$C_{20}H_{18}O_5N_2$	Calc.	C 65.6	H 4.95	N 7.65
	Found	» 65.4	» 4.92	» 7.57

3. 4-Nitro-3-acetaminoretenequinoxaline

0.4 g of 4-nitro-3-acetaminoretenequinone was dissolved in 40 ml of boiling absolute ethanol. A hot ethanol solution containing 0.4 g of o-phenylenediamine was added. Within half a minute the quinoxaline had crystallized out. It was filtered off and washed thoroughly with ethanol in which it is practically insoluble. A recrystallization of the crude product in 200 ml of glacial acetic acid gave a pale yellow product which crystallized as small needles, m. p. 305° C (decomp.). The yield was 0.3 g. The quinoxaline was coloured intensely reddish-brown by concentrated sulphuric acid.

$C_{26}H_{22}O_3N_4$	Calc.	C 71.2	H 5.06
	Found	» 71.1	» 5.08

4. 2-Methylretimidazole-(3′, 4′)

To a mixture consisting of 220 ml of glacial acetic acid and 30 ml of concentrated hydrochloric acid, 35 g of $SnCl_2$ $2H_2O$ and 10 g of 4-nitro-3-acetaminoretene were added. The temperature was raised to 80° C and a weak stream of hydrogen chloride was passed through. As the reduction progressed, an increasing amount of the nitro compound dissolved and the yellow colour shown by the reaction mixture at the beginning finally disappeared. When reduction had continued for 30 mins. and a clear solution was obtained, 45 ml of diluted hydrochloric acid was added. On cooling, short white needle-shaped crystals formed. These were filtered off, washed with diluted hydrochloric acid, water and finally with ether. The yield was 8.9 g. They were then suspended in ether mixed with alkaline (KOH) ethanol. Free imidazole was then obtained. The ether solution was washed with water, dried with sodium sulphate and the ether allowed to evaporate. The residue, which weighed 6.5 g (75 per cent yield) was recrystallized in 150 ml of benzene. The imidazole was obtained as very small, white needle-shaped crystals, m. p. 199.0—199.5° C.

$C_{20}H_{20}N_2$	Calc.	C 83.3	H 6.99	N 9.72
	Found	» 83.4	» 7.07	» 9.64

The foregoing reduction could also be carried out in a solution of ethanol containing hydrochloric acid, giving the same product.

The *picrate* was obtained when a few tenths of a gram of 2-methylretimidazole and 0.5 g of picric acid were boiled in 50 ml of propyl alcohol. A very voluminous yellow picrate was crystallized out of the clear solution. Melting point approx. 272° C (decomp.).

Calc.	C 60.3	H 4.48
Found	» 60.4	» 4.42

The *hydrochloride* crystallized as short needle-shaped crystals from a solution of 2-methylretimidazole in glacial acetic acid to which hydrochloric acid had been added. The hydrochloride was filtered off, washed with glacial acetic acid containing hydrochloric acid, and ether. Melting point > 300 °C. After drying at 130 °C for four hours it was titrated with 0.1 *N* sodium hydroxide.

Calc. Cl 10.92 Found Cl 10.95

5. N-Acetyl-2-methylretimidazole-(3′, 4′)

A few tenths of a gramme of methylretimidazole were boiled in 10 ml of acetic anhydride for 10 minutes and then heated on the water bath for 20 minutes. On cooling, the acetyl derivative crystallized as long needle-shaped crystals which, after recrystallization in acetic anhydride, had a melting point at 202—203 °C.

$C_{22}H_{22}ON_2$	Calc.	C 80.0	H 6.71	N 8.48
	Found	» 80.0	» 6.83	» 8.56

The *picrate* was obtained as small yellow, needle-shaped crystals when an alcoholic solution of picric acid had been added to the acetylretimidazole, dissolved in propyl alcohol. The solutions were mixed hot and boiled for about a minute. Sufficient propyl alcohol was then added to produce complete solution. The picrate is not readily soluble in propyl alcohol. Melting point approx. 269 °C (decomp.).

Calc.	C 60.1	H 4.50
Found	» 59.9	» 4.40

6. 4-Nitro-3-aminoretene

14.8 g of 4-nitro-3-acetaminoretene was suspended in 250 ml of ethanol. 8 g of potassium hydroxide dissolved in 100 ml of water was added and the reaction mixture was heated on the water bath for two hours. A clear dark-red solution was obtained from which long, needle-shaped yellowish-red crystals, m. p. 124—125 °C, crystallized out on cooling. Recrystallization did not raise the melting point. The nitroamine is thus obtained directly in pure form. The yield was 10.0 g, corresponding to 77 per cent of the theoretical.

$C_{18}H_{18}O_2N_2$	Calc.	C 73.5	H 6.16	N 9.52
	Found	» 73.5	» 6.19	» 9.61

The filtrate from the reaction mixture was diluted with water and extracted with ether. When the ether solution had been washed and dried, hydrogen chloride gas was passed through. 1 g of the hydrochloride of the nitroamine was then obtained. This brought the total yield of the nitroamine to 84 per cent.

The *picrate*. An excess of picric acid was added to a solution of 4-nitro-3-aminoretene in ethanol and the solution boiled for about one minute. On cooling, the picrate was obtained as needle-shaped reddish-brown crystals, m. p. 145 °C (decomp.).

Calc.	C 55.1	H 4.04
Found	» 55.3	» 3.98

The *hydrochloride*. Analytically pure 4-nitro-3-aminoretene was dissolved in ether. Hydrogen chloride was passed through and the hydrochloride then precipitated as a pale creamy-yellow product. This was filtered off and dried carefully. It decomposed at approximately 155 °C.

Calc.	C 65.4	H 5.79	Cl 10.72
Found	» 65.1	» 5.89	» 10.62

The chlorine was determined by titration of the hydrochloride with 0.1 *N* sodium hydroxide.

4-Nitro-3-acetaminoretene. 0.1 g of the nitroamine was dissolved in 5 ml of acetic anhydride and heated to boiling point during 10 minutes. A sufficient quantity of water was then cautiously added for the anhydride to be converted into acetic acid. The solution was then allowed to cool. Yellow needle-shaped crystals were obtained which, after recrystallization in glacial acetic acid, melted at 196—197 °C. No depression in the melting point was obtained by mixing with 4-nitro-3-acetaminoretene. The acetylation product is thus 4-nitro-3-acetaminoretene.

7. 3,4-Diaminoretene

1.0 g of 4-nitro-3-aminoretene and 3 g of $Na_2S_2O_4$ were suspended in 25 ml of methanol to which 5 ml of water had been added. The reaction mixture was heated to nearly boiling point during 10 minutes. Decolouration occurred and a practically colourless solution was obtained. A large quantity of the salt remained undissolved. Three times the volume of water was added and the reduction product was extracted with ether. The ether solution was washed with water and dried carefully with sodium sulphate and the ether then distilled off under vacuum. A viscous yellow residue was obtained and recrystallized in petroleum ether (b. p. 40—60 °C) containing 10 per cent benzene. On cooling, the diamine was obtained as needle-shaped crystals melting at 80—81 °C. Further recrystallization did not raise the melting point.

$C_{18}H_{20}N_2$	Calc.	C 81.8	H 7.63	N 10.60
	Found	» 81.8	» 7.65	» 10.52

The *picrate.* 3,4-Diaminoretene was dissolved in boiling ethanol containing 4 g of picric acid in 100 ml of ethanol. The picrate is sparingly soluble in ethanol and relatively large quantities of the solvent are therefore required. The picrate crystallizes as thin, feather-like crystals. It was, however, obtained in such a voluminous form that the contents of the vessel, after cooling, were an almost jelly-like mass. The picrate was filtered off and recrystallized in ethanol. Melting point approx. 165 °C (decomp.). The product was dried at 100 °C for three hours, during which it acquired a greenish colour.

Calc.	C 58.4	H 4.70
Found	» 57.4	» 4.80

The *hydrochloride.* 0.2 g of 3,4-diaminoretene was dissolved in 5 ml of ethanol. Concentrated hydrochloric acid was added in drops. The hydrochloride then crystallized out as flakes with a melting point at 242—244 °C. Titration showed that a dihydrochloride had been formed.

Calc. Cl 21.0 Found Cl 21.0

8. The complex of 3,4-diaminoretene with stannous chloride

0.5 g of 4-nitro-3-aminoretene was dissolved in 10 ml of ethanol. The solution was cooled to approximately 30° C and 2 ml of concentrated hydrochloric acid was added. The faintly creamy-yellow hydrochloride precipitated as a half-solid mass. A solution consisting of 3 g of $SnCl_2 \cdot 2H_2O$, 5 ml of ethanol and 2 ml of concentrated hydrochloric acid was then added. Hydrogen chloride gas was then passed through, the temperature rose to 80° C and a clear solution was formed. After the addition of 30 ml of water, the reaction mixture was allowed to cool. The stannous complex then crystallized as white needle-shaped prisms melting at approximately 190° C (the melting point varies somewhat depending on how long the sample remains in the melting point determination apparatus). The crystals were first washed with dilute hydrochloric acid and then with ether. The yield was 0.6 g, corresponding to 85 per cent.

$C_{36}H_{40}N_4SnCl_2 \cdot 3HCl$	Calc. C 52.3	H 5.23	N 6.77	Sn 14.3	Cl 21.4
	Found » 52.6	» 5.24	» 6.44	» 14.5	» 21.2

The chlorine was determined by titration with 0.1 *N* sodium hydroxide. For the tin determination the sample was first digested by boiling with concentrated sulphuric acid to which some concentrated nitric acid had been added. The tin was then precipitated as a sulphide which was ignited to SnO_2. Direct ignition with sulphuric acid gave considerably lower analytical values (Sn = 13.8 per cent).

This stannous complex could also be produced as follows. 0.1 g of 3,4-diaminoretene was dissolved in 3 ml of ethanol. A solution of 0.5 g of $SnCl_2 \cdot 2H_2O$, 2 ml of ethanol and 0.5 ml of concentrated hydrochloric acid was added and hydrogen chloride gas passed through for a few minutes. The temperature rose to 80° C. After 5 ml of water had been added, the clear solution was allowed to cool. A product similar in appearance to the stannous complex in the foregoing crystallized out. The crystals were filtered off, washed with dilute hydrochloric acid and ether. The melting point was approximately 190° C.

Calc.	C 52.3	H 5.23
Found	» 52.8	» 5.28

If the stannous complex is suspended in ether to which alkaline (KOH) ethanol has been added, the free diamine is formed and obtained according to the way described in the foregoing (v. under 3,4-diaminoretene).

9. Reto-3',4':2,3-reto-9'',10'':5,6-pyrazine

0.3 g of 3,4-diaminoretene was dissolved in 5 ml of ethanol. The solution was mixed with 0.25 g of retenequinone dissolved in 20 ml of absolute ethanol. A dark colouration of the reaction solution could be observed. It was boiled for a few minutes and then allowed to cool. The yellow quinoxaline then precipitated was filtered off and recrystallized twice in dioxane (solubility 1 g in 200 ml). It crystallized as canary-yellow needle-shaped prisms melting at 299—300° C. The yield of the pure product was 0.05 g. The quinoxaline was coloured intensely greenish-blue by concentrated sulphuric acid.

$C_{36}H_{32}N_2$	Calc.	C 87.8	H 6.55	N 5.69
	Found	» 87.3	» 6.44	» 5.61

10. 4-Nitroretene

A solution of 8.0 g of 4-nitro-3-aminoretene in 600 ml of glacial acetic acid was mixed with 185 ml of dilute sulphuric acid consisting of one volume of concentrated acid and three volumes of water. The clear red solution was cooled to + 5° C. The greater part of the sulphate of the nitroamine crystallized out. During 15 minutes a solution of 8 g of sodium nitrite in 35 ml of water was added drop-wise with vigorous stirring. A clear solution was gradually obtained. A reduction solution (see the following) containing hypophosphorous acid was added and the reaction mixture placed in the refrigerator for 20—30 hours. The nitroretene formed on reduction was obtained as a yellow, partly crystalline precipitation. It was filtered off and washed with large quantities of water. The yield was 6.5 g. The crude product was recrystallized in a mixture of 100 ml of absolute ethanol and 20 ml of propyl alcohol. The alcohol solution was boiled with 5 g of charcoal, filtered and allowed to cool. After a further recrystallization and boiling with charcoal, the pure 4-nitroretene was obtained as faintly yellow, long prism-shaped crystals melting at 136—137° C. The yield was 2.5 g. Calculated on the nitroamine this corresponds to a yield of approximately 30 per cent.

$C_{18}H_{17}O_2N$	Calc.	C 77.4	H 6.14	N 5.02
	Found	» 77.3	» 6.05	» 4.99

The 4-nitroretene is readily soluble in boiling glacial acetic acid; 4 g dissolves in less than 10 ml. The solubility in absolute ethanol at boiling point is approximately 1 g in 15 ml.

The reduction solution used in the foregoing was produced as follows. 100 g of dried and pulverised sodium hypophosphite was added in portions to 160 g of concentrated sulphuric acid. When the reaction mixture was left overnight at room temperature, it was diluted with water to a volume of 300 ml and mixed with the diazonium solution.

11. 4-Nitroretenequinone

0.5 g of 4-nitroretene was dissolved in 10 ml of glacial acetic acid. 1.0 g of chromium trioxide was added in portions. When reaction had started, the temperature rose to approximately 100° C on account of the heat of reaction. When oxidation was complete, 35 ml of water was added in drops and with stirring. The quinone was obtained as a flocculent yellow precipitate. It was filtered off and washed carefully with water. After recrystallization, pure quinone was obtained. It crystallized as long yellow needles melting at 185.0—185.5° C.

$C_{18}H_{15}O_4N$	Calc.	C 70.0	H 4.89	N 4.53
	Found	» 70.0	» 4.85	» 4.46

12. 4-Nitroretenequinoxaline

A solution of 0.3 g of 4-nitroretenequinone in 15 ml of ethanol was mixed with a solution of 0.2 g of o-phenylenediamine in 5 ml of ethanol. The mixture was boiled for a few minutes and then allowed to cool. The quinoxaline then crystallized out and was

recrystallized in ligroin (b. p. 65—90° C) containing a small percentage of toluene. It crystallized as faintly yellow, very short needles, melting at 175—176° C. It was coloured reddish-brown by treatment with concentrated sulphuric acid.

$C_{24}H_{19}O_2N_3$	Calc.	C 75.6	H 5.02
	Found	» 75.9	» 5.02

13. 9-Nitro-3-aminoretene

A few tenths of a gram of 9-nitro-3-retylamine hydrochloride were suspended in ether and shaken with a 20 per cent solution of sodium hydroxide. The free nitroamine then dissolved and a faintly yellow ether solution was obtained. This was washed, and dried with sodium sulphate. The ether was distilled off and the blood-red residue was recrystallized twice in ethanol. The nitroamine was obtained as reddish-yellow, needle-shaped crystals, melting at 152—153° C.

$C_{18}H_{18}O_2N_2$	Calc.	C 73.5	H 6.16	N 9.52
	Found	» 73.1	» 6.26	» 9.51

The *picrate* was produced from an ethanol solution in the usual way. 0.3 g of the 9-nitro-3-aminoretene was dissolved together with 0.7 g of picric acid in 50 ml of ethanol and the solution boiled for about one minute. On cooling, the picrate was obtained as thin yellow, needle-shaped crystals with the melting point at 182—183° C (decomp.).

Calc.	C 55.1	H 4.04
Found	» 55.1	» 3.97

For comparison it can be mentioned that the picrate of 4-nitro-3-aminoretene is intensely brown in colour.

9-Nitro-3-acetaminoretene was obtained when the nitroamine was boiled with an excess of acetic anhydride. A clear pale yellow solution was obtained, from which beautiful yellow crystals in the form of flakes were obtained on cooling. Their m. p. was 286—287° C. A mixture with a sample of 9-nitro-3-acetaminoretene [3] gave the same melting point. Since no depression of the melting point was observed, the acetylation product thus consists of 9-nitro-3-acetaminoretene.

SUMMARY

The present investigation is chiefly concerned with a determination of the structure of 4-nitro-3-acetaminoretene. At the same time a series of retene derivatives with some substituent in the 4-position was produced. No 4-derivative of retene has previously been obtained. Among the new retene derivatives special mention is made of 4-nitroretene. Only one nitro derivative of retene is hitherto known, *i. e.* 9-nitroretene. The investigation also in-

cluded the production of 9-nitro-3-aminoretene. This compound has hitherto been assumed to be unstable in air. This is not the case.

The present paper forms a part of a number of investigations with the object of producing a series of nitroretenes. It is thus hoped to throw some light on the problem of nitration of retene.

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