ACTA CHEMICA SCANDINAVICA 4 (1950) 1554–1559

Investigations in the Retene Field

III. 4,9-Dinitroretene

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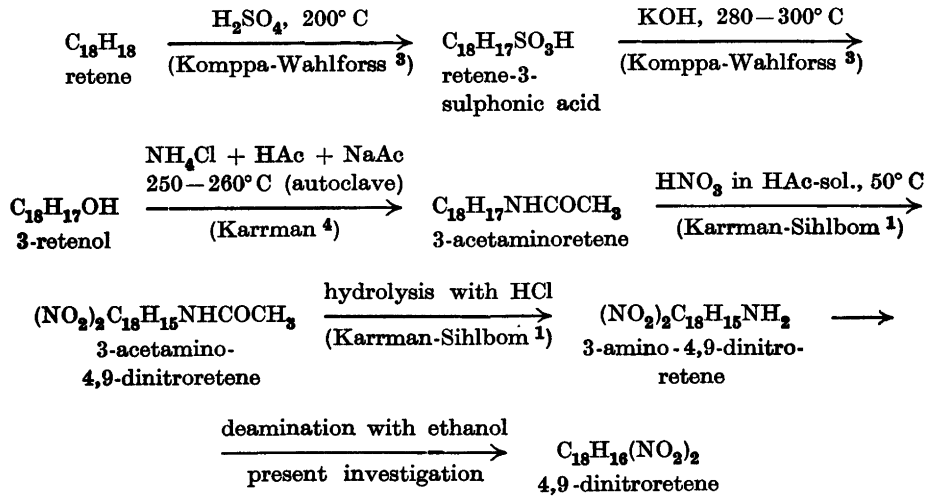
The nitration of 3-acetaminoretene, under mild conditions, yields both 3-acetamino-4-nitroretene and 3-acetamino-9-nitroretene [1-2]. From these derivatives, 4-nitroretene (Sihlbom [2]) and 9-nitroretene (Karrman-Sihlbom [1]) have been prepared. These were the first nitro-derivatives of retene to be synthesized. By utilizing stronger nitrating conditions, a 55 % yield of 3-acetamino-4,9-dinitroretene can be obtained from 3-acetaminoretene [1-2]. In the present paper the preparation of 4,9-dinitroretene from 3-acetamino-4,9-dinitroretene is described.

The following reaction scheme shows the synthesis of 4,9-dinitroretene from retene (the first part of this scheme is also presented in another retene investigation by Karrman-Sihlbom [1]):



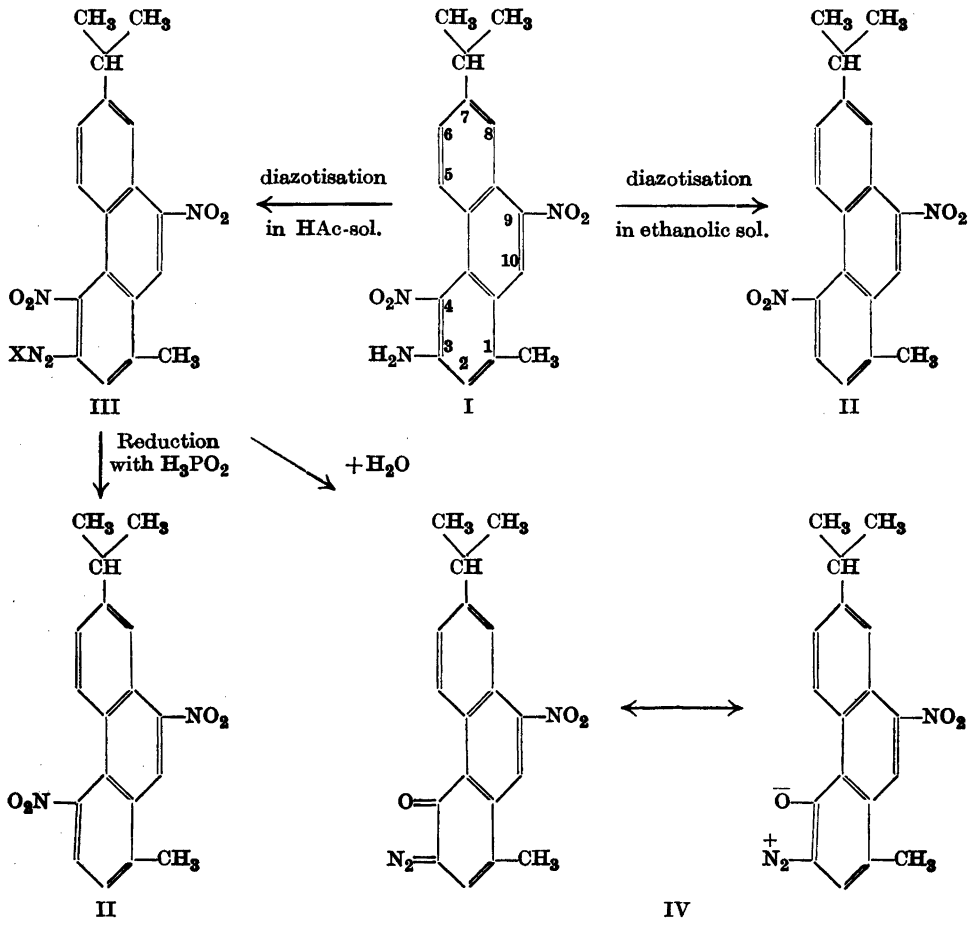
The yield is approximately 10 % for the total synthesis.

The hydrolysis of 3-acetamino-4,9-dinitroretene in ethanol, containing conc. hydrochloric acid, yielded the free amine and not its hydrochloride. This result indicates that the two nitro-groups have considerably reduced the basic characteristics of the amine. Various attempts have been made to obtain the salt of this nitro-amine. If an excess of conc. sulphuric acid is added to a warm solution of the amine in either ethanol or glacial acetic acid, the amine sulphate crystallizes on cooling. The acetic acid solution requires a relatively small excess of sulphuric acid.

If an excess of conc. hydrochloric acid is added to the warm glacial acetic acid solution, the nitro-amine decomposes. In this solution, it appears as if the hydrochloric acid causes a nitro-group to split off. At the same time, a diazonium salt is formed which then gradually decomposes. This reaction will be discussed further in a later paper. — If conc. hydrochloric acid is added to a cool solution of the nitro-amine in glacial acetic acid, the amine hydrochloride can be obtained.

As can be seen from the reaction scheme below, 4,9-dinitroretene (II) has been prepared by the deamination of 3-amino-4,9-dinitroretene (I). The diazonium salt (III) was reduced with hypophosphorous acid or ethanol. The latter reducing agent is preferable, as the reaction solution should contain as little water as possible. The presence of water causes the diazonium salt to decompose into a brick-red product, probably 9-nitroretene-3-diazo-4-oxide (IV). This substance is apparently decomposed by light, since exposure to daylight for some hours causes the colour to change from brick-red to grey. In the dark, the colour does not change even after a considerable time. The diazo-oxide is slightly soluble in the usual organic solvents and decomposes violently on heating. An ethanolic solution of the diazo-oxide gives a green colour with an alkaline resorcinol solution. These proporties are in agreement with those expected for a diazo-oxide [5]. This substance will be further discussed in a later publication. — Other examples of the formation of diazo-oxides from aqueous solutions of diazonium salts of nitro-amines, are given by Kornblum in *Organic reactions* [6].

In view of the abovementioned characteristics of the nitro-amine and its diazonium salt, the deamination was accomplished in ethanol in the presence of a large amount of sulphuric acid. The nitrous acid was added as nitrosyl sulphuric acid. The diazonium salt is reduced as fast as it is formed, to 4,9-dinitroretene (II) which precipitates and can easily be removed by filtration. The crude product obtained was purified by chromatography. Pure dinitroretene was obtained in a yield of 72 %, calculated on the nitro-amine consu-



med. By the chromatographic purification, 15 % of unreacted nitro-amine was also isolated.

The reduction of 4,9-dinitroretene with stannous chloride yielded the corresponding diamine. This was obtained in the form of a difficultly soluble tin complex which, contrary to the corresponding complex of 3,4-diaminoretene [2], precipitated in a very impure form and was therefore not further examined. In order to obtain the free amine, the tin complex was suspended in ether and washed with an aqueous alkali solution. These reactions must be accomplished in a nitrogen atmosphere, since the amine solution otherwise becomes a deep red colour. The 4,9-diaminoretene has been characterized by the following simple derivatives: the hydrochloride, the trinitrobenzene double compound, the picrate, and the N,N'-diacetyl compound.

EXPERIMENTAL

4,9-Dinitroretene

5.0 g of 3-amino-4,9-dinitroretene was dissolved in 700 ml of boiling ethanol. The solution was cooled to 50° C when 200 ml of conc. sulphuric acid was added with cooling and stirring. When the solution was cooled to 5—10° C, rather large quantities of amine sulphate separated as crystals. At this temperature, a solution of 2.5 g of sodium nitrite in 35 ml of conc. sulphuric acid was added, with stirring, in the course of one hour. The diazonium salt formed was rapidly reduced by the ethanol to 4,9-dinitroretene, which was obtained as a yellow flocculent precipitate. The reduction was complete after the addition of the nitrite solution (no coupling reaction with β-naphtol). In order to assure complete precipitation, approx. 1 000 ml of water was added. The yield of crude product was 4.4 g. This was dissolved in a mixture of 75 ml of benzene and 75 ml of ligroin (b. p. 65—90° C). A little residue remained undissolved. From the dark solution, 4,9-dinitroretene and unchanged nitro-amine were isolated chromatographically. The solution was taken up in a column of alumina, 30 cm high and 3.5 cm diameter. On passing a mixture of 2 vol. of benzene and 3 vol. of petroleum ether (b. p. 40—60° C), 4,9-dinitroretene moves through the column as a faintly yellow band. From the percolate 2.9 g of completely pure dinitroretene (m. p. 170—171° C) was isolated. Recrystallization did not raise the melting point. *n*-Propanol is a suitable recrystallization solvent; in 100 ml of *n*-propanol 6 g of the compound can be dissolved at the boiling point and 0.5 g at 10° C. The compound is also readily soluble in acetone, benzene, and chloroform, slightly soluble in ligroin and ethanol. It crystallizes from propanol as pale-yellow needles.

$C_{18}H_{16}N_2O_4$ (324.3)	Calc.	C 66.6	H 4.97	N 8.64
	Found	» 66.8	» 5.04	» 8.72

In the chromatographic purification there was also formed a sharp reddish-brown band which moved very slowly through the column. After the addition of pure benzene, the chromatogram was better developed, and from the reddish-brown band 0.8 g of 3-amino-4,9-dinitroretene was isolated. Therefore, the yield of 4,9-dinitroretene, based on the amount of nitro-amine actually consumed, is 72 %.

9-Nitroretene-3-diazo-4-oxide

0.5 g of 3-amino-4,9-dinitroretene was dissolved in 80 ml of warm glacial acetic acid. 1 ml of conc. sulphuric acid was added and the solution was cooled to about 20° C. Most of the amine sulphate separated as nearly colourless crystals. A small excess of 20 % sodium nitrite solution was added. The clear diazonium salt solution was diluted with 80 ml of water. Almost immediately a brick-red precipitate began to separate. After 30 minutes it was filtered off, and washed with dilute acetic acid, ethanol, and ether. On heating it decomposes explosively and shows no definite melting point.

$C_{18}H_{15}N_3O_3$ (321.3)	Calc.	C 67.3	H 4.71	N 13.08
	Found	« 66.6	» 4.71	» 12.50

The colour of the diazo-oxide changes from brick-red to grey when exposed to daylight for about 6 hours. An ethanolic solution of the diazo-oxide gives a green colour with an alkaline resorcinol solution.

4,9-Diaminoretene

16 g of $SnCl_2 . 2H_2O$ was dissolved in 45 ml of glacial acetic acid containing hydrogen chloride. With cooling and stirring, 2.0 g of finely powdered 4,9-dinitroretene was added in small portions. The temperature was kept at about 20° C. As the reduction proceeds, 4,9-dinitroretene gradually dissolves, but a clear solution is not obtained because a white fine-grained product begins to separate before all the dinitroretene is reduced. After one hour, when the reduction was complete, the reaction mixture was saturated with hydrogen chloride and the precipitate was filtered off. This precipitate consists of tin salts and a tin salt complex of 4,9-diaminoretene (a pure tin salt complex like that of 3,4-diaminoretene [2] is not easily obtained in this case). Yield about 2.7 g. — As a solution of the diamine in ether turns red in the presence of air, the following operations were performed in a nitrogen atmosphere. — A suspension of the crude product in ether was shaken with a 10 % sodium hydroxide solution containing a few tenths of a gram of sodium hydrosulfite. After washing and drying the ether solution, the solvent was evaporated. The residue, a faintly reddish-brown viscous oil, soon crystallized forming a pale-yellow crystalline mass. Yield 1.1 g, corresponding to 67.5 % of the theoretical. One recrystallization from a mixture of 4 ml of benzene and 10 ml of ligroin (b. p. 65—90° C) yielded 0.9 g of the pure product, m. p. 114—115° C. It is readily soluble in ethanol, acetic acid, and benzene, slightly soluble in ligroin. 4,9-diaminoretene crystallizes as nearly colourless plates.

$C_{18}H_{20}N_2$ (264.4)	Calc.	C 81.8	H 7.63	N 10.60
	Found	» 82.1	» 7.60	» 10.45

The *hydrochloride* was obtained as white needle-shaped crystals when conc. hydrochloric acid was added to a solution of 4,9-diaminoretene in ethanol. The compound has no definite melting point. It gradually decomposes and turns dark at about 150° C. Titration showed that a dihydrochloride had been formed.

$C_{18}H_{22}N_2Cl_2$ (337.3) Calc. Cl 21.0 Found Cl 21.3

The *picrate.* 0.1 g of 4,9-diaminoretene was dissolved in 3 ml of hot ethanol containing 0.15 g of picric acid. On cooling, the picrate crystallized as flat yellow prisms. At 135° C it begins to decompose rather rapidly, but there is no definite melting point.

$C_{24}H_{23}N_5O_7$ (493.5)	Calc.	C 58.4	H 4.70
	Found	» 57.6	» 4.86

The *trinitrobenzene double compound* is very rapidly formed when two etanolic solutions containing sym. trinitrobenzene and 4,9-diaminoretene, respectively, are mixed. The double compound is only slightly soluble in ethanol, but can be recrystallized from this solvent. It crystallizes as long thin needles with dark greyish-brown colour. M. p. 224—225° C (decomp.).

$C_{24}H_{23}N_5O_6$ (477.5)	Calc.	C 60.4	H 4.85
	Found	» 60.3	» 4.81

N, N'-Diacetyl-4,9-diaminoretene. 1.0 g of 4,9-diaminoretene was dissolved in 25 ml of 80 % acetic acid. Two hours after the addition of 2 ml of acetic anhydride, the diacetyl compound formed was filtered off. Yield 0.9 g. M. p. 299—300° C. Recrystallization did not raise the melting point. Thus the compound is obtained directly in a pure state. It is slightly soluble in ethanol and benzene, and somewhat more soluble in glacial acetic acid. The substance crystallizes as short white needles.

$C_{22}H_{24}N_2O_2$ (348.4)	Calc.	C 75.8	H 6.94
	Found	» 75.8	» 6.98

SUMMARY

4,9-Dinitroretene and the corresponding 4,9-diaminoretene have been synthesized from 3-amino-4,9-dinitroretene. Some simple derivatives of the diamine have been prepared.

In the course of these syntheses it was found that the diazonium salt of 3-amino-4,9-dinitroretene is hydrolyzed by water to a brick-red substance, probably 9-nitroretene-3-diazo-4-oxide.

It has also been found that 3-amino-4,9-dinitroretene, dissolved in hot glacial acetic acid, reacts with conc. hydrochloric acid forming a diazonium salt. It may be assumed that the first step of this intramolecular diazotization is the replacement of one of the two nitro-groups by chlorine.

I wish to express my gratitude to *Stiftelsen Bokförlaget Natur och Kultur* for financial support.

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Received October 19, 1950.