

Retene Investigations

X. Oxidation of Retene with Hydrogen Peroxide

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Oxidation of retene to well defined products offers serious difficulties. Potassium permanganate has no effect either in acid or alkaline solution¹. With diluted nitric acid a mixture of different nitro-compounds is obtained and possibly carboxylic acids as well². With potassium ferricyanide the side chains are oxidized to carboxyl groups³, but this treatment is not practical and the yield is small. The best known and most widely used oxidizing agent is chromic acid in glacial acetic acid which converts retene to retene quinone with a yield of 35—40 %⁴. Bichromates, on the other hand, give a very low yield of quinone.

From a technical point of view the use of chromic acid and glacial acetic acid proves too expensive especially when the relatively poor yield of quinone is taken into consideration. Retene quinone in itself is not a product of technical use but only as an intermediate useful for the manufacture of dyes, dicarboxylic acids, etc. We, therefore, considered it suitable to make a more systematic investigation of the possibilities of oxidizing retene to carboxylic acids in a more satisfactory manner.

Hydrogen peroxide was chosen as oxidizing agent on the grounds that its technical significance is constantly increasing. It is now produced industrially at as high a concentration as 90 %. Hydrogen peroxide is seldomly used for oxidation of hydrocarbons but in the literature, however, we have found a few examples of such oxidations. Thus, there is a statement to the effect that phenanthrene can be oxidized with hydrogen peroxide to diphenic acid⁵. Cyclo-hexane is oxidized by hydrogen peroxide to cyclo-hexandiol in the presence of selenium dioxide⁶.

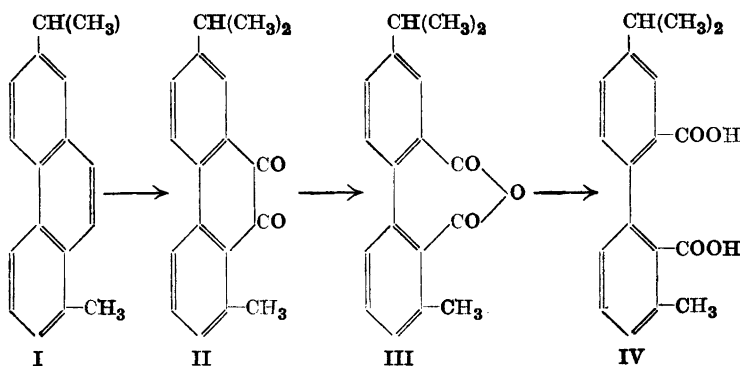
It is generally known that ortho-quinones may be oxidized with hydrogen peroxide with the formation of dicarboxylic acids⁷. In this manner, also

retene quinone has been oxidized. This oxidation was first carried out by Bamberger and Hooker⁸, who, however, failed to obtain any crystalline acid, and later by Fogelberg⁹, who succeeded in obtaining retenediphenic acid in crystalline form. He obtained after the oxidation a sticky mass which was converted to the anhydride. After hydrolysis of the anhydride the crystalline acid was obtained. Finally Adelson, Hasselstrom and Bogert¹⁰ have worked out a method which gives retenediphenic acid in a yield of 65 % from retene quinone. But since retene quinone is only obtained in a yield of approximately 40 % from retene, the yield of retenediphenic acid from retene is only 20—25 %. The object of this investigation is the production of retenediphenic acid in a better yield from retene by oxidation with hydrogen peroxide.

OXIDATION OF RETENE IN GLACIAL ACETIC ACID SOLUTION

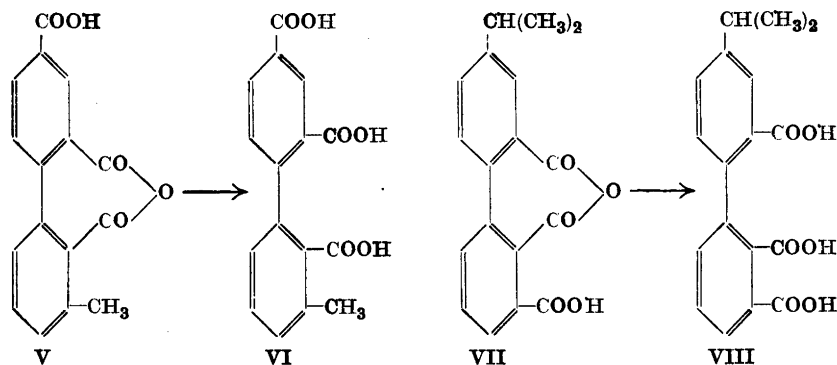
Hydrogen peroxide reacts very strongly with retene dissolved in glacial acetic acid. The reaction mixture first turns dark red, but after a few hours it takes on a lighter colour. According to Charrier and Moggi⁵, who investigated the oxidation of phenanthrene, this phenomenon may be explained by supposing that quinone-like products are initially formed and that these are then oxidized to carboxylic acids. As a matter of fact we have isolated carboxylic acids from the crude reaction product at approximately 90 % yield. The acid fraction purified by conversion to the anhydride turned out, for the most part, to be retene-diphenic acid (IV).

The reaction may be supposed to take place in the following manner. In the first stage of oxidation retene quinone as indicated by the red colour is presumably formed. In the reaction product we have, however, also noted retenediphenic acid anhydride and it is possible that the anhydride is not only a by-product but also a genuine intermediary product of the oxidation of retene to retenediphenic acid. In this respect it is interesting to note that by the oxidation of camphor quinone with hydrogen peroxide, camphoric acid anhydride is the principal product. It seems, therefore, likely that the reaction takes place mainly in the following manner:



If the oxidation product is extracted with a bicarbonate solution and the diphenic acid is then precipitated with sulphuric acid, a smaller quantity of diphenic acid is obtained than when the reaction product is boiled first with sodium hydroxide, and then the acid precipitated. Retenediphenic acid anhydride, being relatively stable, reacts very slowly with bicarbonate solution.

The crude reaction product is more or less dark coloured and of resinous appearance and cannot be brought to crystallization. It may also be assumed that the side chains are partially oxidized to carboxyl groups, since the analysis of the crude acid reveals a higher content of oxygen than that calculated for retenediphenic acid. The fact that the equivalent weight is higher than calculated may be explained by assuming that a part of the reaction product consists of anhydride acids. The presence of the following anhydride acids (V and VII) is very likely.



If the crude oxidation product is boiled with alkali, lower values for the equivalent weight are found. This can only be explained by assuming that the above-named anhydride acids are saponified to tribasic acids (VI and VIII). When all these things are taken into consideration the quantity of anhydride acids is relatively small compared to the quantity of retenediphenic acid. We have not succeeded in isolating the anhydride acids in a pure state.

OXIDATION IN ETHANOL AND DIOXANE SOLUTION IN THE PRESENCE OF SELENIUM DIOXIDE

If one attempts to oxidize retene with hydrogen peroxide in ethanol solution no oxidation takes place and one obtains for the most part unchanged retene. Almost the same result is obtained in dioxane solution, the yield of acids being extremely poor. If, on the other hand, retene is oxidized with hydrogen peroxide in the two solvents mentioned above and in the presence

of small quantities of selenium dioxide, retenediphenic acid is obtained in quite a good yield. Selenium dioxide, therefore, has a very obvious effect on the oxidation of retene. As oxidation in glacial acetic acid (acid medium) runs smoothly even in the absence of selenium dioxide, it might be surmised that the effect of selenium dioxide depends solely on the fact that it acidifies the reaction mixture when ethanol and dioxane are used as solvents. That this is not the case was clearly demonstrated by experiments with sulphuric acid instead of selenium dioxide. No oxidation was observed (table 1).

Table 1. Oxidation of retene with hydrogen peroxide in different solvents.

Solvents	Added substance (in small quantities)	Reaction products in %		
		Unchanged retene	Neutr. oxidation products	Acid. oxidation products
Ethanol	—	95	—	2
•	SeO ₂	—	35	90
•	H ₂ SO ₄	95	—	2
Dioxane	—	90	—	10
•	SeO ₂	—	10	85
Acetic acid	—	—	10	90
• •	SeO ₂	—	20	85

In acetic acid solution selenium dioxide has, as mentioned above, no noticeable influence on the oxidation. The neutral oxidation products contain approx. 13 % oxygen, the acids approx. 24 %.

OXIDATION OF PHENANTHRENE

In the literature we have only found one reference which deals with the oxidation of phenanthrene with hydrogen peroxide⁵. For the sake of comparison, therefore, we considered it to be of interest to carry out a few oxidation experiments with phenanthrene. The conditions in this case are much simpler than with retene, since the formation of anhydride acids (V and VII) is of course excluded. We immediately obtained diphenic acid in crystalline form. From the fraction of the oxidation products which is insoluble in bicarbonate we have isolated diphenic acid anhydride. This supports the above-mentioned conclusion concerning the course of the oxidation. If the oxidations of phenanthrene and retene are compared it is found that retene gives a higher yield of acids than phenanthrene. This is shown in table 2.

Table 2. Oxidation of retene and phenanthrene with hydrogen peroxide in glacial acetic acid.

Substance	Oxidation product in percentage of the theoretical yield	
	Neutral	NaHCO ₃ -soluble
Phenanthrene	25	50
Retene	10	90

SOME DERIVATIVES OF RETENEDIPHENIC ACID

Seeing that retenediphenic acid has now become a readily available substance, we considered it appropriate to prepare from it a few simple derivatives which have not been prepared previously.

Neutral methyl esters. Neutral esters of retenediphenic acid and simple aliphatic alcohols have not previously been prepared. On the other hand, Adelson and others¹⁰ prepared glyptal-like esters from retenediphenic acid and glycerol or borneol, obtaining light brown, resin-like masses.

Retenediphenic acid reacts easily with methanol with the formation of the acid ester. To prepare the neutral ester a solution of retenediphenic acid in methanol was saturated with hydrochloric acid and then boiled for several hours. But in spite of the fact that the neutral esters may be easily prepared in this manner from both phthalic acid¹¹ and diphenic acid¹², we obtained from retenediphenic acid the neutral ester in a yield of only approximately 25%. Therefore the chloride of retenediphenic acid was first prepared with phosphorous pentachloride and then the chloride was reacted with methanol. In this manner the neutral ester was obtained in a yield of approx. 70%.

It is likely that the presence of a methyl group in ortho-position to one of the carboxyl group has a hindering effect on its esterification.

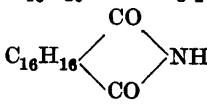
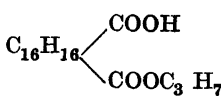
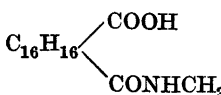
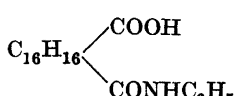
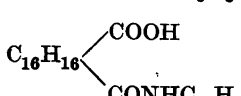
The neutral methyl ester of retenediphenic acid has the consistency of a thick oil which does not appear to crystallize.

The *imide* was obtained by heating the monoamide, the latter being formed by the reaction of ammonia and retenediphenic acid anhydride.

Different amines react easily with retenediphenic anhydride to form the N substituted monoamides. In this manner we have prepared methyl, phenyl and naphthyl derivatives.

Bromination of retenediphenic acid anhydride gave a monobromo derivative. Although the analysis agrees with the calculated values it is presumably a mixture of isomers because the melting-point is far from sharp. On saponification more alkali is consumed than theoretically calculated and a quantity bromine is split off.

Summary of newly prepared substances.

Name	Formula	Property
Retenediphenic acid dimethyl ester	$C_{16}H_{16}(COOCH_3)_2$	light yellow oil
» » imide	$C_{16}H_{16}$ 	—
» » monopropyl ester	$C_{16}H_{16}$ 	sticky mass
» » methylamide	$C_{16}H_{16}$ 	m. p. 165—166° C
» » anilide	$C_{16}H_{16}$ 	m. p. 251—252° C
» » α -naphthyl amide	$C_{16}H_{16}$ 	m. p. 125—127° C

EXPERIMENTAL

Oxidation of retene with hydrogen peroxide in glacial acetic acid

25 g retene were dissolved in 100 ml warm glacial acetic acid and to the boiling solution were added 70 ml 30 % hydrogen peroxide in small quantities. The mixture was boiled for 12 hours. The solution was first very dark red, but grew considerably lighter toward the conclusion of boiling. The solvent was first evaporated under ordinary pressure and then *in vacuo*. The residue, 30.8 g, was divided into two equal parts (15.4 g each).

I. The one half was boiled with sodium hydroxide.

1. Neutral oxidation product 1.2 g (not investigated).

2. Acid oxidation product 14.1 g (= 90 %, assuming that the whole is retenediphenic acid, $C_{18}H_{18}O_4$).

$C_{18}H_{18}O_4$	Calc. C	72.5	H	6.08	O	21.5 (diff.)	Equiv.wt.	149
	Found »	70.0	»	5.91	»	24.1	»	»
								144

Both the equivalent weight determined by titration and the elementary analysis (oxygen excess) show that a quantity of tri- or quadribasic acids is present (oxidation of side chains).

II. The second half was boiled with a bicarbonate solution.

1. Neutral oxidation product 4.4 g (not investigated).
2. Acid oxidation product 10.9 g (= 70 %, assuming that the whole is retenediphenic acid).

The greater quantity of the neutral part in this case shows that anhydride is present in the reaction product.

The acid fraction was analysed:

$C_{18}H_{18}O_4$	Calc. C 72.5	H 6.08	O 21.5 (diff.)
	Found » 71.5	» 5.83	» 22.7 »

Titration (direct) gave an equiv. weight of 178, calc. 149 (for retenediphenic acid). After boiling with sodium hydroxide an equivalent weight of 145 was found. This indicates as mentioned above the presence of anhydride or possibly a lactone group.

Preparation of the anhydride

40 g of the oxidation product soluble in alkali was boiled with 80 ml acetic acid anhydride for 2 hours under reflux. After the solvent had been removed, 36 g of reaction product were obtained. The product was crystallized from ether. (Yield 22 g.) After recrystallization from acetic acid a pure product was obtained with m. p. 111—112° C. Retenediphenic acid anhydride melts according to Fogelberg at 111—112° C.

$C_{18}H_{16}O_3$	Calc. C 77.1	H 5.76
	Found » 77.0	» 5.77

The retenediphenic acid anhydride was boiled with sodium hydroxide, after which the equiv. weight agreed with the calculated value. The melting-point for the retenediphenic acid thus obtained (187—189° C) agrees with the values in the literature.

Oxidation in ethanol and dioxane solutions

5 g of retene dissolved in 80 ml of ethanol or dioxane were boiled with 20 ml 30 % hydrogen peroxide for 20 hours with or without addition of small quantities of selenium dioxide or sulphuric acid. Retene, when precipitated, was filtered off, the solvent evaporated, and the residue treated first with bicarbonate solution and then with a solution of sodium hydroxide. The solutions were then acidified with sulphuric acid and the precipitated acids dissolved in ether. In this manner the quantities of neutral oxidation products and of oxidation products soluble in bicarbonate were determined. (See table 1.)

Dimethyl ester of retenediphenic acid

1. *Boiling with methanol containing hydrochloric acid.* 10 g of retenediphenic acid were dissolved in 50 ml of methanol and the solution was saturated with gaseous hydrochloric acid at 0° C. The reaction mixture was allowed to stand over night, after which it was boiled for 3 hours under reflux. The remaining methanol was distilled off and the residue dissolved in ether. The ethereal solution was first washed with water and later with a bicarbonate solution. This was finally acidified and the precipitated oil collected in ether. In this manner the neutral and the acid esterification products were separated from one

another; (yield 2.3 g and 7.2 g respectively). The neutral part containing dimethyl ester was distilled at 1 mm Hg 230—250° C. A light-brown viscous oil was obtained.

$C_{20}H_{22}O_4$	Calc. C 73.6	H 6.80
	Found » 74.2	» 6.94

2. *Esterification with acid chloride.* 5.0 g of retenediphenic acid (crude product) and 7.0 g of phosphorous pentachloride were heated in a waterbath and boiled until the gas evolution had ceased and a clear solution was formed. The reaction mixture was allowed to react with methanol for 3 hours. After the remaining methanol had been distilled off, the residue was dissolved in ether and the ether solution washed with water and a solution of bicarbonate. After the ether had been distilled off, the residue was distilled at 1 mm Hg (230—250° C). Yield 3.4 g of a light brown oil (68 % of the theoretical yield).

$C_{20}H_{22}O_4$	Calc. C 73.6	H 6.80
	Found » 73.0	» 6.65

n-Propyl ester, $C_{16}H_{16}$ $\begin{cases} \text{COOC}_3\text{H}_7 \\ \text{COOH} \end{cases}$ To 1 g of retenediphenic acid anhydride was added

an excess of *n*-propyl alcohol and the mixture was boiled for a short time. After the solvent had been evaporated, a tough, almost colourless mass was obtained, which could not be crystallized.

	Calc. C 74.0	H 7.11
	Found » 73.3	» 7.03

N-Phenyl retenediphenicamide, $C_{16}H_{16}$ $\begin{cases} \text{CONHC}_6\text{H}_5 \\ \text{COOH} \end{cases}$ Equal parts of retenediphenic acid

anhydride and aniline were heated together, after which the excess of aniline was removed with diluted hydrochloric acid. The crude product was recrystallized from ethanol. M. p. 251—252° C.

	Calc. C 77.2	H 6.21
	Found » 77.2	» 6.14

N- α -Naphthyl retenediphenicamide, $C_{16}H_{16}$ $\begin{cases} \text{CONHC}_{10}\text{H}_7 \\ \text{COOH} \end{cases}$ was obtained in a similar manner from retenediphenic acid anhydride and α -naphthyl amine. M. p. 125—127° C.

	Calc. C 79.4	H 5.96
	Found » 79.2	» 5.82

N-Methyl retenediphenicamide, $C_{16}H_{16}$ $\begin{cases} \text{CONHCH}_3 \\ \text{COOH} \end{cases}$ was obtained from methylamine

hydrochloride and retenediphenic acid anhydride in the presence of an excess of alkali. The crude product was recrystallized from ethanol. M. p. 165—166° C.

Calc. C	73.3	H	6.80
Found	» 72.9	»	» 6.64

Oxidation of phenanthrene. 5 g of phenanthrene, 50 ml of glacial acetic acid and 25 ml 30 % hydrogen peroxide were boiled for three hours. The neutral and acid fractions of the reaction products were isolated in the previously described manner. Yield: neutral fraction 1.4 g, acid fraction 3.7 g. The acid reaction product was analysed.

Diphenic acid, C ₁₄ H ₁₀ O ₄	Calc. C	69.4	H	4.17
	Found	» 69.4	»	» 4.17

On titration 88.6 mg of substance consumed 7.25 ml of 0.1007 *N* sodium hydroxide, theoretical value for C₁₄H₁₀O₄, 7.20 ml.

Both from the analysis and the titration it is clear that a very pure diphenic acid is immediately obtained by the oxidation of phenanthrene. The melting point of diphenic acid was 227—228° C as compared to 228—229° C as reported in the literature⁹.

SUMMARY

Retene, dissolved in acetic acid, was oxidized by hydrogen peroxide to a dibasic acid, retenediphenic acid, in a yield of approx. 70 %. In ethanol or dioxane solution retene was oxidized only in the presence of small quantities of selenium dioxide. Selenium dioxide has no effect on the oxidation of retene in acetic acid solution.

Some simple derivatives of retenediphenic acid have been prepared.

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