

A METHOD FOR AN OXIDIZING HYDROLYSIS OF OZONIDES PREPARED FROM UNSATURATED ACIDS

J. L. RIEBSOMER and RALPH C. TALLMAN,¹ DePauw University

Most vegetable fats and oils contain glycerides of unsaturated acids—some with only a small percentage, and others consist almost entirely of unsaturated materials. It is only the unsaturated acids with which this paper deals.

Ozone has been used since about 1900 for the determination of the structure of such acids. The general procedure has been to dissolve the acid in some solvent such as chloroform or acetic acid, pass ozone through the solution, and then to hydrolyze the resulting ozonide. This hydrolysis breaks the molecule into fragments at the positions of the unsaturated linkages:

Harries² did the pioneer work in this field. This investigator hydrolyzed the ozonide simply by boiling it with water. In working with an acid containing one double bond, this procedure would produce two aldehydes and two acids and necessitate the separation of four constituents, which might create quite a problem especially when small amounts are involved.

Noller and Adams³ have hydrolyzed such ozonides under reducing conditions using zinc dust. This method produces two aldehydes from an unsaturated acid containing one multiple linkage. These investigators, however, were chiefly interested in the aldehyde ester for synthetic purposes. They found it possible to get yields as high as 60 to 70 per cent of fairly pure products. Upon repeated distillation of the aldehyde ester it was found that polymerization took place resulting in high boiling materials. Furthermore, the aldehyde groups readily oxidized to the corresponding acids upon standing in the air which resulted in a mixture of products. From an analytical standpoint these things are objectionable.

In our efforts to find a method of hydrolysis for ozonides which would give satisfactory yields and which would be as simple in application as possible, hydrogen peroxide was added to some ozonides in acetic acid solution and the hydrolysis carried out in this oxidizing medium. Hydrogen peroxide was given preference over dichromate and permanganate and other common oxidizing agents because it leaves nothing but water to remove from the mixture.

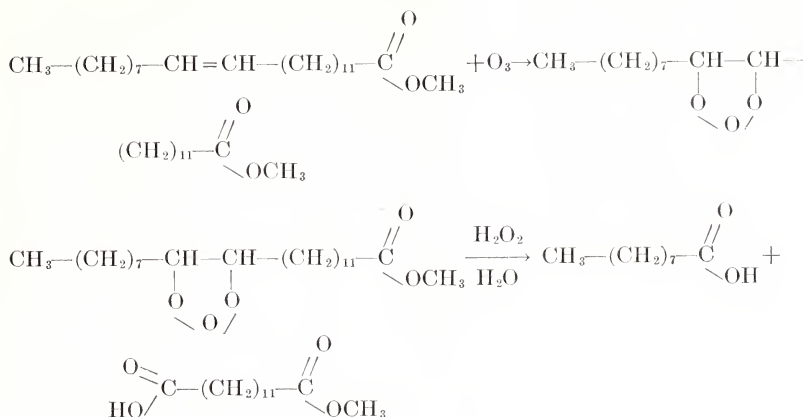
When this reaction was carried out, the fragments of the molecules were converted to the acids, the yields were as high as 62 per cent of the theoretical, and the separation of the products simplified.

This method was carried out using methyl erucate for which the reactions may be represented as follows:

¹ Dr. Tallman is an instructor of organic chemistry at Cornell University, Ithaca, New York. This work was carried out with him at that institution.

² Harries, *Ber.*, **39**:3732 (1906).

³ Noller and Adams, *J. Am. Chem. Soc.*, **48**:1074 (1926).



This method has been used successfully in the study of the oil from *Lycopodium* spores⁴, and in the investigation of pumpkin seed oil (Unpublished). Furthermore, the method applied to methyl oleate is being used as a laboratory exercise for students of organic chemistry. This procedure is not only of value for analytical purposes but may be used for the preparation of shorter chain fatty acids for which there is not always an adequate and inexpensive supply.

EXPERIMENTAL

Two hundred grams of erucic acid obtained from The Eastman Kodak Company was converted to the methyl ester by refluxing the acid with ten times the theoretical amount of methyl alcohol containing 4 cc. of concentrated sulphuric acid. After refluxing for five hours most of the excess methyl alcohol was distilled from the mixture over a steam bath. The ester was then washed, first with water to remove the sulphuric acid, then with a solution of 1 per cent sodium carbonate, and finally with a cold 1 per cent solution potassium hydroxide until all the unreacted acid had been removed. The ester was taken up in ether, dried with anhydrous magnesium sulphate and then distilled at 2.5 mm. pressure using an ordinary Claisen flask. At this pressure 198 grams of the ester boiled from 213-217°C. This represented 95 per cent of the theoretical yield.

Ninety-four grams of the methyl erucate thus prepared was dissolved in an approximately equal volume of dry acetic acid (note 1, at end of paper) placed in a round-bottomed flask with a ground glass joint and treated with ozone using the apparatus described by Henne⁵. Ozone was passed through until a small test sample did not decolorize a dilute solution of bromine in glacial acetic acid.

When this test indicated that ozone absorption was complete, the acetic acid solution of the ozonide was transferred to a 500 cc. flask connected with a condenser by means of a ground glass joint, note 2,

⁴ Riebsomer and Johnson, J. Am. Chem. Soc., 35:2 (1933).

⁵ Henne, J. Am. Chem. Soc., 51:2676 (1929).

and 60 grams of hydrogen peroxide (30 per cent aqueous solution) was added. The mixture was heated over a steam bath for four to five hours, note 3, and finally over a low flame until all the peroxide was decomposed. The complete decomposition of the peroxide was indicated by adding a drop of the mixture to starch-iodide paper. When the test failed to give the usual blue color the reaction was completed.

This mixture contained water, acetic acid, pelargonic acid, and mono-methyl brassylate. To remove the water about 600 cc. of dry benzene was added, the whole placed in a round-bottomed flask to which was attached a Wurtz fractionating column. The flask was then heated in an oil bath which caused the benzene-water mixture to distill, note 4.

Acetic acid was removed from the mixture by transferring the dried liquid from above to a Claisen distilling flask, and distilling at a pressure of 40 mm. using an oil bath which was heated to a maximum of 110°C, note 5.

This procedure left in the distilling flask a small quantity of acetic acid, pelargonic acid, and mono-methyl brassylate. In order to convert the acid ester to the methyl esters, this mixture was treated with methyl alcohol according to the procedure indicated above for the conversion of erucic acid to the methyl ester.

After drying the esters so produced, the mixture was fractionally distilled using a modified Claisen flask, with the following results:

Fraction	Pressure (mm.)	Temperature °C.	Grams Distillate
1	3.5	69-72	28.5
2	3.5	72-160	3.5
3	3.5	160-162.5	45.0
4	3.0	161-190	8.0
Residue			

Fraction 1 proved to be methyl pelargonate and fraction 3 was dimethyl brassylate. The weights indicated above represent slightly better than 62 per cent of the theoretical yield of each of the products.

NOTES ON PROCEDURE

1. The dry acetic acid was prepared by adding excess acetic anhydride to ordinary glacial acetic acid and refluxing for two to three hours.

2. An ordinary flask and condenser may be used if the stopper is well wrapped with tin foil.

3. When heating of the ozonide and hydrogen peroxide mixture is started, care must be used to prevent the reaction from becoming too vigorous.

4. If the water was not all removed by the first distillation, more benzene was added and the process repeated.

5. Pelargonic acid distills at 110°C at a pressure of two millimeters; little was lost by this procedure.

SUMMARY

1. A detailed procedure for the oxidizing hydrolysis of unsaturated fatty acid ozonides has been presented.
2. This method has been used successfully in the solution of problems involving the determination of structure of naturally occurring unsaturated acids.
3. The procedure is simple in practice. It has been used successfully in the hands of elementary organic chemistry students.

SOME EXPERIMENTS IN COLORING CELLOPHANE

LOUIS A. TEST, Purdue University

As is well known cellophane may be easily and attractively colored by many organic dyes, all the direct cotton dyes being taken up very readily. Mention in the literature of any attempts to use inorganic substances for a similar purpose seem to be lacking.

The experiments here described were undertaken at the suggestion of Mr. R. B. Withrow of the Horticultural Department of Purdue University who was carrying on an investigation to determine the effect of artificial light on plant growth. Colored cellophane had been used to modify the quality of the light. As the organic dyes do not absorb the extreme red end of the spectrum satisfactorily, the thought occurred that inorganic colors might serve better. Mr. Withrow had used cellophane screens colored with Prussian blue in some of his work, the results of which are soon to be published. His preliminary experiments with Prussian blue showed that cellophane could be colored with inorganic substances, the desired colored substance being formed directly in the cellophane.

The cellophane used in these experiments was Dupont's number 600, which is about twice as heavy as that used for ordinary commercial wrappings. The preliminary experiments with Prussian blue seemed to indicate that the colored compound was formed in the cellophane in a colloidal condition and was not deposited on the surface. This led to the belief that those substances which easily entered into the colloidal state might give the most satisfactory results.

The general method of procedure was to soak the cellophane in water until free from glycerine. The wet cellophane was then placed for a few minutes in a dilute solution, usually 1 or 2 per cent of one of the reacting substances. On removal from this solution the excess of reagent was washed from the surface with running water, the cellophane immediately immersed in a solution of the necessary reagent to produce the desired compound and left as long as the color continued to develop. Finally it was washed in running water. If the color was not as intense as desired the process was repeated until the desired intensity was obtained.